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(54) Title: COPOLYMERIC COMPOUNDS COMPRISING ONE OR MORE ACTIVE ALDEHYDE MONOMERIC UNIT		
(57) Abstract		
The present invention relates to copolymeric compound comprising one or more active ingredient. By the present invention, a delayed release of the active ingredient is provided upon contact of the compound with an aqueous medium.		

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COPOLYMERIC COMPOUNDS COMPRISING ONE OR MORE ACTIVE ALDEHYDE MONOMERIC UNIT

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10

Field of the invention

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The present invention relates to co-polymeric compounds comprising one or more active aldehyde monomeric unit. More particularly, it relates to polymeric compounds of aldehyde active monomeric unit and glyoxylic monomeric unit for
20 use in laundry and cleaning products as well as personal care compositions.

25

Background of the invention

30

Cleaning and laundry products are well-known in the art. However, consumer acceptance of laundry and cleaning products is determined not only by the performance achieved with these products but also the aesthetics associated therewith. The perfume components are therefore an important aspect of the
35 successful formulation of such commercial products.

35

It is also desired by consumers for laundered fabrics to maintain the pleasing fragrance over time. Indeed, perfume additives make laundry compositions more aesthetically pleasing to the consumer, and in some cases the perfume imparts a pleasant fragrance to fabrics treated therewith. However, the amount of perfume

carry-over from an aqueous laundry bath onto fabrics is often marginal and does not last long on the fabric. Furthermore, fragrance materials are often very costly and their inefficient use in laundry and cleaning compositions and ineffective delivery to fabrics result in a very high cost to both consumers and laundry and cleaning manufacturers. Industry, therefore, continues to seek with urgency for more efficient and effective fragrance delivery in laundry and cleaning products, especially for improvement in the provision of long-lasting fragrance to the fabrics.

5 10 One solution is to use carrier mechanisms for perfume delivery, such as by encapsulation. This is taught in the prior art and described in U.S. 5,188,753. Still another solution is to formulate compounds which provide a delayed release of the perfume over a longer period of time than by the use of the perfume itself have been provided. Disclosure of such compounds may be found in WO 15 95/04809, WO 95/08976 and pending application EP 95303762.9.

However, notwithstanding the advances in the art, there is still a need for a compound which provides a delayed release of the perfume component.

20 25 The Applicant has now found that co-polymeric compounds comprising one or more active aldehyde ingredient also provide a delayed release of the active such as a perfume.

Another advantage of the invention is that it allows the incorporation of a high proportion of active aldehyde into a polymeric compound. Preparing a polymer of an active aldehyde alone would be highly desirable for the controlled release of said active aldehyde. However, it is known to the persons skilled in the art that these poly(active aldehyde) can not be easily obtained by direct polymerisation of one or more active aldehydes alone. The applicants have found that the polymerisation of a suitable comonomer along with the active aldehydes allow them to incorporate a high proportion of one or more active aldehydes into a polymeric compound. Had the co-monomer not been present, no incorporation of the aldehyde into a polymeric compound would have taken place, under the same conditions.

Still another advantage of the present invention is that by choosing the suitable co-monomeric unit and end-capping groups, it provides sufficient stabilisation of the linkage bond between the active aldehyde group with its polymeric carrier so that the release of the active ingredients upon storage in product is limited,

5 without hindering the release of the active ingredients upon use of the product.

Still another advantage of the invention compounds is their ease of manufacture rendering their use most desirable.

10

Summary of the invention

15 The present invention relates to a co-polymeric compound comprising one or more active aldehyde ingredient, wherein said compound has the following empirical formula:
-[Y_m-A_n]-
wherein Y is a comonomeric aldehyde unit of formula R'COH,
20 wherein R' is the organic chain of an active aldehyde,
wherein A is a comonomeric unit capable of polymerising the aldehyde monomeric unit, and
wherein n and m are each independently indexes of value of at least 1.

25 In another aspect of the invention, there is provided a laundry and cleaning composition or personal cleansing composition comprising said compound.

Still another aspect of the invention is a method of delivering residual fragrance to a surface which comprises the steps of contacting said surface with a
30 compound of the invention or a composition comprising said compound in presence of a material so that the copolymer backbone is hydrolysed, thereby slowly releasing overtime the perfume aldehydes.

Detailed description of the invention

5 The essential component of the invention is a co-polymeric compound comprising one or more active aldehyde ingredient. The compound of the invention has the following empirical formula:

-[Y_m-A_n]-

wherein Y is a co-monomeric aldehyde unit of formula R'COH,
wherein R' is the organic chain of an active aldehyde,

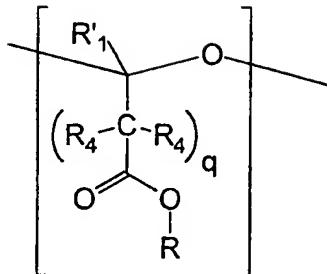
10 wherein A is a co-monomeric unit capable of polymerising the aldehyde monomeric unit, and
wherein n and m are each independently indexes of value of at least 1, preferably less than 1000, most preferably less than 100.

15 Preferably, the ratio n/m is greater than 1, most preferably greater than 3.

By "co-monomeric unit", it is meant any suitable comonomer which can be copolymerised with the aldehyde monomeric unit. Typical of such comonomers are those having at least two reactive sites and which do not inhibit the 20 polymerisation or cause the copolymer to depolymerise in alkaline solution. Preferably, these monomeric units are selected from keto carboxylates R',OC(CR₄R₄)_qCOOR and among keto carboxylates more preferably glyoxylates (R'1 =H, q=0) or α -keto malonates (R'1 =COOR, q=0).

25 For ease of purpose, the copolymer has been schematised under its empirical formula as a block copolymer. However, it will be obvious for those skilled in the art that, in general, by copolymerisation of two or more different monomers, the copolymer obtained generally show a completely random distribution of the monomers along the backbone of the polymer rather than the block distribution
30 represented above. Any combination possible of the different monomers in the copolymer will not affect the overall controlled release benefit observed with such copolymer and are therefore included in the present description.

Preferred co-monomeric unit A capable of polymerising the aldehyde monomeric
35 unit is keto carboxylate monomeric unit of formula:



wherein each R is independently selected from hydrogen, alkali metals, ammonium, alkyl, alkylene, aryl, alkylaryl, or any other chain containing at least 1 carbon atom;

5 wherein each R'1 is independently selected from hydrogen, hydroxyl, alkyl, alkylene, aryl, alkylaryl, COOR3, (CR4R4)_qCOOR3, OR3, or any other chains containing at least 1 carbon atom;

wherein each R3 is independently selected from hydrogen, alkali metals, ammonium, alkyl, alkylene, aryl, alkylaryl, or any other chain containing at least 1

10 carbon atom, and

wherein each R4 are independently selected from hydrogen, hydroxyl, alkyl, alkylene, aryl, alkylaryl, COOR3, CH₂COOR3, OR3, or any other chain containing at least 1 carbon atom; and

wherein q is from 0 to 10, preferably from 0 to 4, more preferably 0, 1 or 2.

15

Most preferred co-monomeric keto carboxylate unit A capable of polymerising the aldehyde monomeric unit is a glyoxylic monomeric unit of formula:

20 wherein each R is independently selected from hydrogen, alkali metals, ammonium, alkyl, alkylene, aryl, alkylaryl, or any other chain containing at least 1 carbon atom;

wherein each R'1 is independently selected from hydrogen, hydroxyl, alkyl, alkylene, aryl, alkylaryl, COOR3, OR3, or any other chains containing at least 1

25 carbon atom;

wherein each R3 is independently selected from hydrogen, alkali metals, ammonium, alkyl, alkylene, aryl, alkylaryl, or any other chain containing at least 1 carbon atom, and

wherein q is 0.

30

Preferably, for the above keto carboxylate and glyoxylic monomeric unit, the R groups are each independently selected from alkali metals, ammonium, C1-C6 alkyl chains, and more preferably are selected from methyl and ethyl.

5 The preferred R'1 groups are each independently selected from hydrogen, -COOR3, (CR₄R₄)_qCOOR3, aryl group, and C1-C6 alkyl chains, and more preferably are selected from hydrogen, -COOR3, phenyl, methyl and ethyl.

10 The preferred R3 groups are each independently selected from hydrogen, alkali metals, ammonium, aryl group and C1-C6 alkyl chains, and more preferably are selected from hydrogen, alkali metals, ammonium, methyl and ethyl.

15 The preferred R4 are each independently selected from hydrogen, -COOR3, aryl group and C1-C6 alkyl chains, and more preferably is selected from hydrogen, phenyl, methyl and ethyl.

By alkyl and alkenyl chain, it is understood a chain length of at least 1 carbon, preferably 1 to 20 carbon atoms, and more preferably is methyl or ethyl.

20 Of course, it is also understood that the chain and cycles can be optionally substituted or interrupted. Typical of such substitution is a short alkyl chain such as methyl, ethyl, or hydroxy group. Typical of such interruption is with an O, N, CO, OC(O), CO(O), C(O)N, NC(O) and mixtures thereof.

25 For the above mentioned compounds, by "organic chain" of an active aldehyde, it is meant any chain containing at least 1 carbon atom, preferably at least 5 carbon atoms. Preferably, the active aldehyde is respectively selected from a flavour aldehyde ingredient, a pharmaceutical aldehyde active, a biocontrol aldehyde agent, a perfume aldehyde component and mixtures thereof. When more than one organic chain of an active aldehyde is present on the compound 30 of the invention, each organic chain of an active aldehyde can be different from the others, e.g. when there are two organic chain of an active aldehyde, one can be a biocontrol aldehyde agent and the other a perfume aldehyde component, or one organic chain of an active aldehyde is a perfume aldehyde component and the other organic chain of an active aldehyde a different perfume aldehyde 35 component.

Flavour ingredients include spices, flavor enhancers that contribute to the overall flavour perception.

Pharmaceutical actives include drugs.

5

Biocontrol agents include biocides, antimicrobials, bactericides, fungicides, algaecides, mildewcides, disinfectants, antiseptics, insecticides, vermicides, plant growth hormones.

10 Perfume aldehyde components include components having odoriferous properties.

Preferably, for the above mentioned compounds, the R' group is the organic chain of a perfume aldehyde, said aldehyde being selected from 2,6,10-trimethyl-9-undecenal, 3-dodecen-1-al, alpha-n-amyl cinnamic aldehyde, 4-methoxybenzaldehyde, benzaldehyde, 3-(4-tert butylphenyl)-propanal, 2-methyl-3-(para-methoxyphenyl) propanal, 2-methyl-4-(2,6,6-trimethyl-2(1)-cyclohexen-1-yl) butanal, 3-phenyl-2-propenal, cis-/trans-3,7-dimethyl-2,6-octadien-1-al, 3,7-dimethyl-6-octen-1-al, [(3,7-dimethyl-6-octenyl)oxy] acetaldehyde, 4-isopropylbenzylaldehyde, 1,2,3,4,5,6,7,8-octahydro-8,8-dimethyl-2-naphthaldehyde, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, 2-methyl-3-(isopropylphenyl)propanal, 1-decanal; decyl aldehyde, 2,6-dimethyl-5-heptenal, 4-(tricyclo[5.2.1.0(2,6)]-decylidene-8)-butanal, octahydro-4,7-methano-1H-indenecarboxaldehyde, 3-ethoxy-4-hydroxy benzaldehyde, para-ethyl-alpha, alpha-dimethyl hydrocinnamaldehyde, alpha-methyl-3,4-(methylenedioxy)-hydrocinnamaldehyde, 3,4-methylenedioxymethylbenzaldehyde, alpha-n-hexyl cinnamic aldehyde, m-cymene-7-carboxaldehyde, alpha-methyl phenyl acetaldehyde, 7-hydroxy-3,7-dimethyl octanal, Undecenal, 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde, 4-(3)(4-methyl-3-pentenyl)-3-cyclohexen-30 carboxaldehyde, 1-dodecanal, 2,4-dimethyl cyclohexene-3-carboxaldehyde, 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde, 7-methoxy-3,7-dimethyloctan-1-al, 2-methyl undecanal, 2-methyl decanal, 1-nonanal, 1-octanal, 2,6,10-trimethyl-5,9-undecadienal, 2-methyl-3-(4-tertbutyl)propanal, Phenylacetaldehyde, dihydrocinnamic Aldehyde, 1-methyl-4-(4-methyl-3-pentenyl)-3-cyclohexene-1-carboxaldehyde, 5 or 6 methoxyhexahydro-4,7-methanoindan-1 or 2- carboxaldehyde, 3,7-dimethyloctan-1-al, 2,4-dimethyl-3-

cyclohexene-1-carboxaldehyde, 1-undecanal, 10-undecen-1-al, 4-hydroxy-3-methoxy benzaldehyde, 1-methyl-3-(4-methylpentyl)-3-cyclhexenecarboxaldehyde, 2,4-dimethyl-3-cyclohexene-1-carboxaldehyde, 7-hydroxy-3,7-dimethyl-octanal, trans-4-decenal, 2,6-nonadienal, para-tolylacetaldehyde; 4-methylphenylacetaldehyde, 2-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butenal, ortho-methoxycinnamic aldehyde, 3,5,6-trimethyl-3-cyclohexene carboxaldehyde and 2,4,6-trimethyl-3-cyclohexene carboxaldehyde, 3,7-dimethyl-2-methylene-6-octenal, Phenoxyacetaldehyde, 5,9-dimethyl-4,8-decadienal, Peony Aldehyde (6,10-dimethyl-3-oxa-5,9-undecadien-1-al), hexahydro-4,7-methanoindan-1-carboxaldehyde, 2-methyl octanal, alpha-methyl-4-(1-methyl ethyl) benzene acetaldehyde, 6,6-dimethyl-2-norpinene-2-propionaldehyde, para methyl phenoxy acetaldehyde, 2-methyl-3-phenyl-2-propen-1-al, 3,5,5-trimethyl hexanal, Hexahydro-8,8-dimethyl-2-naphthaldehyde, 3-propyl-bicyclo[2.2.1]-hept-5-ene-2-carbaldehyde, 9-decenal, 3-methyl-5-phenyl-1-pentanal, methylnonyl acetaldehyde, benzaldehyde, and mixtures thereof.

Most preferred aldehydes are selected from 1-octanal, 1-decanal, 1-dodecanal, methylnonyl acetaldehyde, trans-4-decenal, benzaldehyde and mixture thereof.

20 For the purpose of the invention, mixtures of the above compounds comprising one or more active aldehydes may also be used.

Mechanism of release

25 By the present invention, a delayed release of an active ingredient, i.e. aldehyde is obtained. Not to be bound by theory, the release is believed to occur by the following mechanism:
For copolymers or oligomers of active aldehydes and of suitable comonomers such as keto carboxylates (in particular glyoxylic esters), the active aldehydes
30 are released upon breaking down of the acetals bond forming the backbone of the polymer, leading to the release of the active aldehyde and of the suitable comonomers. This can be achieved by either hydrolysis, photochemical cleavage, enzymatic cleavage or oxidative cleavage of the bond linking the end-capping group to the rest of the polymer or any acetal bonds along the polymer
35 backbone.

Process

Preparation of the component is made as follows in the Synthesis Examples. In general, process for preparing a copolymer comprising one or more active aldehydes comprises the steps of polymerising one or more active aldehydes 5 with one or more suitable comonomers, preferably keto carboxylates, most preferably glyoxylates such as methyl glyoxylate, in presence of a polymerisation catalyst, preferably a strong Lewis acid such as boron trifluoride diethyl etherate or an anionic catalyst such as sodiomalonates or sodiomethylmalonate esters.

10 Preferred features of these general processes for manufacturing the present compounds invention are described hereinafter.

A preferred process for preparing copolymers of one or more active aldehydes:

(A)- to bring together under polymerisation conditions one or more active 15 aldehydes with one or more comonomers capable of polymerising the aldehyde monomeric unit, in presence of a polymerisation initiator; and

(B)- End-capping the resulting copolymer with a suitable chemical group so that the in-product stability of the polymer can be optimised to prevent excessive depolymerisation in-product.

20 As described hereinbefore, the preferred comonomers capable of polymerising the aldehyde monomeric unit are the α -keto carboxylates, most preferably the methyl glyoxylate.

25 Suitable initiator for the copolymerisation are known to those skilled in the art and described in the art such as in US 4,204,052 Column 4, lines 3-15. Preferred initiators are phosphorus pentoxide, amines, strong Lewis acid such as boron trifluoride diethyl etherate, hydroxide or cyanide ions or anionic catalyst such as sodiomalonates or sodiomethylmalonate esters. Most preferred initiators are 30 phosphorus pentoxide, amines, strong Lewis acid such as boron trifluoride diethyl etherate, or anionic catalyst such as sodiomalonates or sodiomethylmalonate esters.

The copolymerisation step can be done with or without solvent. Suitable 35 solvents include alkyl nitriles, preferably acetonitrile, dimethyl sulfoxide, acetone, halogenated alkanes, preferably dichloromethane or chloroform, tetrahydrofuran,

ethyl acetate and the like. When a solvent is used, the choice of the solvent is driven, so that it does not interfere with the copolymerisation and can be separated from the resulting copolymer with relative ease. These solvents can also be used for the end-capping step (B). Dichloromethane and acetonitrile are
5 the preferred solvents for both steps (A) and (B) of the process.

Once the copolymer of one or more active aldehydes and at least one suitable comonomer has been prepared, any number of chemically reactive groups can be added to the copolymer termini, preferably using an ionic catalyst such as
10 boron trifluoride etherate, trifluoroacetic acid and the like as described in US 4,204,052 Column 5 line 25 to Column 6 line 28.

The resulting co-polymer has the following empirical formula:
R1-[Y_m-A_n]-R2
15 wherein Y, A, m and n are as defined hereinbefore; and
wherein R1 and R2 are end-capping groups.

Particularly suitable end-capping groups include alkyl groups, alkyl groups containing oxygen such as -CH₂CHOH or alkoxy, preferably methoxy, or ethers
20 such as -CH(CH₃)-O-CH₂CH₃, -OCH₂CHOH and -OCH(CH₃)-O-CH₂CH₃, and alkyl groups containing carboxylic acids. Particularly preferred end-capping groups for the purpose of the invention are alkyl groups containing oxygen, preferably selected from -CH₂CHOH, -CH(CH₃)-O-CH₂CH₃, -OCH₂CHOH and -OCH(CH₃)-O-CH₂CH₃. As will occur to those skilled in the art in light of the
25 present disclosure, the chemically stable end groups at the polymer termini can be like or unlike.

The chemical nature of the chemically reactive group is not important in the proper function of the copolymer in its intended use to release active aldehydes.
30 It is only necessary that the chemically reactive group stabilises the copolymer so that to limit the depolymerisation before use. The end-capping group can be chosen so that depolymerisation upon usage is triggered by either hydrolysis, photochemical cleavage, enzymatic cleavage or oxidative cleavage of the bond linking the end-capping group to the rest of the polymer or any acetal bonds
35 along the polymer backbone.

Laundry and cleaning compositions

The present invention compositions include both laundry and cleaning compositions which are typically used for laundering fabrics and cleaning hard surfaces such as dishware, floors, bathrooms, toilet, kitchen and other surfaces

5 in need of a delayed release of an active alcohol or mixed alcohol/aldehyde. This also includes compositions for use in personal cleansing such as shower gels, deodorants, bars, shampoos.

Preferred are those laundry compositions which result in contacting the

10 compound of the invention with fabric. Preferably, for use in such laundry and cleaning products, the active alcohol is a perfume such as geraniol.

These are to be understood to include not only detergent compositions which provide fabric cleaning benefits, but also compositions such as rinse added fabric

15 softener compositions and dryer added compositions (e.g. sheets) which provide softening and/or antistatic benefits as well as hard surface cleaning.

The compound(s) of the invention typically comprise from 0.01% to 10%, preferably from 0.05% to 5%, and more preferably from 0.1% to 2%, by weight of

20 the composition. Mixtures of the compounds may also be used herein.

Optional ingredients useful for formulating such laundry and cleaning compositions according to the present invention include one or more of the following.

25

Fabric Softening Agents:

A fabric softener component may also suitably be used in the laundry and cleaning compositions of the invention so as to provide softness and antistatic properties to the treated fabrics. When used, the fabric softener component will

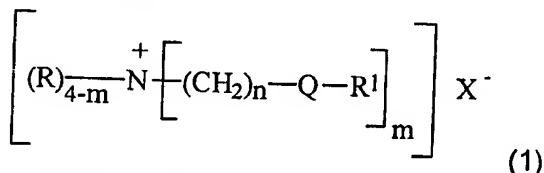
30 typically be present at a level sufficient to provide softening and antistatic properties.

Said fabric softening component may be selected from cationic, nonionic, amphoteric or anionic fabric softening component.

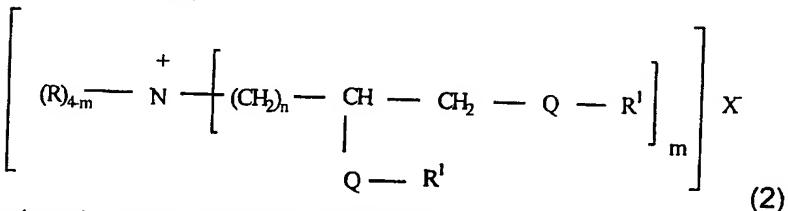
Typical of the cationic softening components are the quaternary ammonium compounds or amine precursors thereof as defined hereinafter.

A)-Quaternary Ammonium Fabric Softening Active Compound

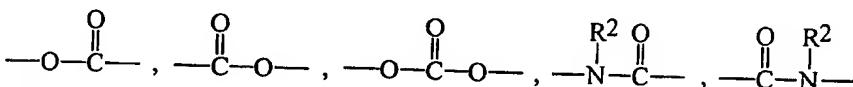
5 (1) Preferred quaternary ammonium fabric softening active compound have the formula



or the formula:

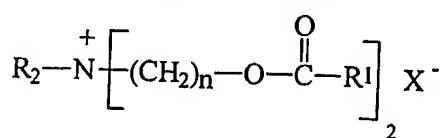


10 wherein Q is a carbonyl unit having the formula:



each R unit is independently hydrogen, C₁-C₆ alkyl, C₁-C₆ hydroxyalkyl, and mixtures thereof, preferably methyl or hydroxy alkyl; each R¹ unit is independently linear or branched C₁₁-C₂₂ alkyl, linear or branched C₁₁-C₂₂ alkenyl, and mixtures thereof, R² is hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and mixtures thereof; X is an anion which is compatible with fabric softener actives and adjunct ingredients; the index m is from 1 to 4, preferably 2; the index n is from 1 to 4, preferably 2.

15 20 An example of a preferred fabric softener active is a mixture of quaternized amines having the formula:

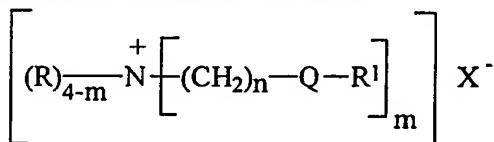


wherein R is preferably methyl; R¹ is a linear or branched alkyl or alkenyl chain comprising at least 11 atoms, preferably at least 15 atoms. In the above fabric softener example, the unit -O₂CR¹ represents a fatty acyl unit which is typically derived from a triglyceride source. The triglyceride source is preferably derived

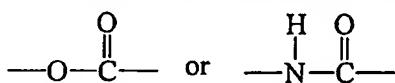
from tallow, partially hydrogenated tallow, lard, partially hydrogenated lard, vegetable oils and/or partially hydrogenated vegetable oils, such as, canola oil, safflower oil, peanut oil, sunflower oil, corn oil, soybean oil, tall oil, rice bran oil, etc. and mixtures of these oils.

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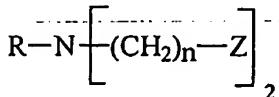
The preferred fabric softening actives of the present invention are the Diester and/or Diamide Quaternary Ammonium (DEQA) compounds, the diesters and diamides having the formula:



10 wherein R, R¹, X, and n are the same as defined herein above for formulas (1) and (2), and Q has the formula:



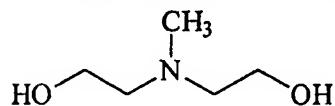
These preferred fabric softening actives are formed from the reaction of an amine with a fatty acyl unit to form an amine intermediate having the formula:



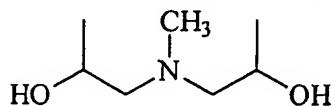
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wherein R is preferably methyl, Z is -OH, -NH₂, or mixtures thereof; followed by quaternization to the final softener active.

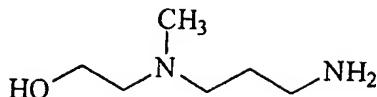
20 Non-limiting examples of preferred amines which are used to form the DEQA fabric softening actives according to the present invention include methyl bis(2-hydroxyethyl)amine having the formula:



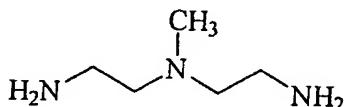
methyl bis(2-hydroxypropyl)amine having the formula:



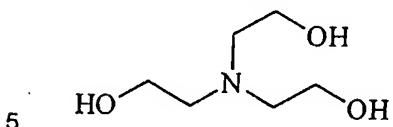
25 methyl (3-aminopropyl) (2-hydroxyethyl)amine having the formula:



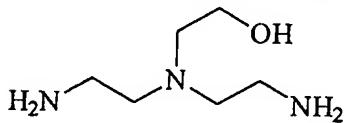
methyl bis(2-aminoethyl)amine having the formula:



triethanol amine having the formula:



5 di(2-aminoethyl) ethanolamine having the formula:



The counterion, X^- above, can be any softener-compatible anion, preferably the anion of a strong acid, for example, chloride, bromide, methylsulfate, ethylsulfate, sulfate, nitrate and the like, more preferably chloride or methyl sulfate. The anion can also, but less preferably, carry a double charge in which case X^- represents half a group.

Tallow and canola oil are convenient and inexpensive sources of fatty acyl units
15 which are suitable for use in the present invention as R^1 units. The following are non-limiting examples of quaternary ammonium compounds suitable for use in the compositions of the present invention. The term "tallowyl" as used herein below indicates the R^1 unit is derived from a tallow triglyceride source and is a mixture of fatty acyl units. Likewise, the use of the term canolyl refers to a
20 mixture of fatty acyl units derived from canola oil.

Table II
Fabric Softener Actives

N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
25 N,N-di(canolyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium
chloride;

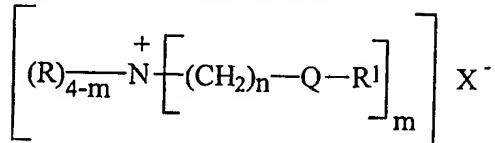
N,N-di(canolyloxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium chloride;
N,N-di(2-tallowyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
N,N-di(2-canolyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride
5 N,N-di(2-tallowyloxyethylcarbonyloxyethyl)-N,N-dimethyl ammonium chloride;
N,N-di(2-canolyloxyethylcarbonyloxyethyl)-N,N-dimethyl ammonium chloride;
N-(2-tallowyloxy-2-ethyl)-N-(2-tallowyloxy-2-oxo-ethyl)-N,N-dimethyl
10 ammonium chloride;
N-(2-canolyloxy-2-ethyl)-N-(2-canolyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
N,N,N-tricanolyloxy-ethyl)-N-methyl ammonium chloride;
15 N-(2-tallowyloxy-2-oxoethyl)-N-(tallowyl)-N,N-dimethyl ammonium chloride;
N-(2-canolyloxy-2-oxoethyl)-N-(canolyl)-N,N-dimethyl ammonium chloride;
1,2-ditallowyloxy-3-N,N,N-trimethylammoniopropane chloride; and
1,2-dicanolyloxy-3-N,N,N-trimethylammoniopropane chloride;
20 and mixtures of the above actives.

Other examples of quaternary ammonium softening compounds are methylbis(tallowamidoethyl)(2-hydroxyethyl)ammonium methylsulfate and methylbis(hydrogenated tallowamidoethyl)(2-hydroxyethyl)ammonium methylsulfate; these materials are available from Witco Chemical Company under the trade names Varisoft® 222 and Varisoft® 110, respectively.

Particularly preferred is N,N-di(tallowoyl-oxy-ethyl)-N,N-dimethyl ammonium chloride, where the tallow chains are at least partially unsaturated.

30 The level of unsaturation contained within the tallow, canola, or other fatty acyl unit chain can be measured by the Iodine Value (IV) of the corresponding fatty acid, which in the present case should preferably be in the range of from 5 to 100 with two categories of compounds being distinguished, having a IV below or
35 above 25.

Indeed, for compounds having the formula:



derived from tallow fatty acids, when the Iodine Value is from 5 to 25, preferably 15 to 20, it has been found that a *cis/trans* isomer weight ratio greater than 5 30/70, preferably greater than 50/50 and more preferably greater than 70/30 provides optimal concentrability.

For compounds of this type made from tallow fatty acids having a Iodine Value of above 25, the ratio of *cis* to *trans* isomers has been found to be less critical unless very high concentrations are needed.

10 Other suitable examples of fabric softener actives are derived from fatty acyl groups wherein the terms "tallowyl" and canolyl" in the above examples are replaced by the terms "cocoyl, palmyl, lauryl, oleyl, ricinoleyl, stearyl, palmityl," which correspond to the triglyceride source from which the fatty acyl units are derived. These alternative fatty acyl sources can comprise either fully saturated, 15 or preferably at least partly unsaturated chains.

As described herein before, R units are preferably methyl, however, suitable fabric softener actives are described by replacing the term "methyl" in the above examples in Table II with the units "ethyl, ethoxy, propyl, propoxy, isopropyl, 20 butyl, isobutyl and t-butyl.

The counter ion, X, in the examples of Table II can be suitably replaced by bromide, methylsulfate, formate, sulfate, nitrate, and mixtures thereof. In fact, the anion, X, is merely present as a counterion of the positively charged 25 quaternary ammonium compounds. The scope of this invention is not considered limited to any particular anion.

For the preceding ester fabric softening agents, the pH of the compositions herein is an important parameter of the present invention. Indeed, it influences 30 the stability of the quaternary ammonium or amine precursors compounds, especially in prolonged storage conditions.

The pH, as defined in the present context, is measured in the neat compositions at 20 °C. While these compositions are operable at pH of less than 6.0, for optimum hydrolytic stability of these compositions, the neat pH, measured in the

above-mentioned conditions, must preferably be in the range of from 2.0 to 5, preferably in the range of 2.5 to 4.5, preferably 2.5 to 3.5. The pH of these compositions herein can be regulated by the addition of a Bronsted acid.

Examples of suitable acids include the inorganic mineral acids, carboxylic acids, 5 in particular the low molecular weight (C₁-C₅) carboxylic acids, and alkylsulfonic acids. Suitable inorganic acids include HCl, H₂SO₄, HNO₃ and H₃PO₄. Suitable organic acids include formic, acetic, citric, methylsulfonic and ethylsulfonic acid. Preferred acids are citric, hydrochloric, phosphoric, formic, methylsulfonic acid, and benzoic acids.

10

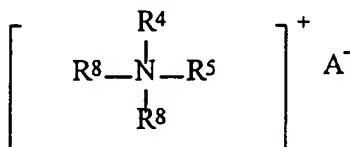
As used herein, when the diester is specified, it will include the monoester that is normally present in manufacture. For softening, under no/low detergent carry-over laundry conditions the percentage of monoester should be as low as possible, preferably no more than 2.5%. However, under high detergent 15 carry-over conditions, some monoester is preferred. The overall ratios of diester to monoester are from 100:1 to 2:1, preferably from 50:1 to 5:1, more preferably from 13:1 to 8:1. Under high detergent carry-over conditions, the di/monoester ratio is preferably 11:1. The level of monoester present can be controlled in the manufacturing of the softener compound.

20

Mixtures of actives of formula (1) and (2) may also be prepared.

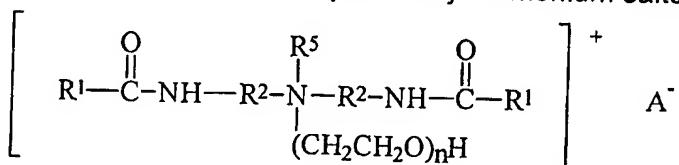
2)-Still other suitable quaternary ammonium fabric softening compounds for use herein are cationic nitrogenous salts having two or more long chain acyclic 25 aliphatic C₈-C₂₂ hydrocarbon groups or one said group and an arylalkyl group which can be used either alone or as part of a mixture are selected from the group consisting of:

(i) acyclic quaternary ammonium salts having the formula:



wherein R⁴ is an acyclic aliphatic C₈-C₂₂ hydrocarbon group, R⁵ is a C₁-C₄ saturated alkyl or hydroxyalkyl group, R⁸ is selected from the group consisting of R⁴ and R⁵ groups, and A- is an anion defined as above;

(ii) diamino alkoxylated quaternary ammonium salts having the formula:



5 wherein n is equal to 1 to 5, and R¹, R², R⁵ and A⁻ are as defined above;
 (iii) mixtures thereof.

Examples of the above class cationic nitrogenous salts are the well-known dialkyldimethylammonium salts such as ditallowdimethylammonium chloride, 10 ditallowdimethylammonium methylsulfate, di(hydrogenatedtallow)dimethylammonium chloride, distearyldimethylammonium chloride, dibehenyldimethylammonium chloride. Di(hydrogenatedtallow)dimethylammonium chloride and ditallowdimethylammonium chloride are preferred. Examples of commercially available dialkyldimethyl ammonium salts usable in 15 the present invention are di(hydrogenatedtallow)dimethylammonium chloride (trade name Adogen® 442), ditallowdimethylammonium chloride (trade name Adogen® 470, Praepagen® 3445), distearyl dimethylammonium chloride (trade name Arosurf® TA-100), all available from Witco Chemical Company. Dibehenyldimethylammonium chloride is sold under the trade name Kemamine 20 Q-2802C by Humko Chemical Division of Witco Chemical Corporation. Dimethylstearylbenzyl ammonium chloride is sold under the trade names Varisoft ® SDC by Witco Chemical Company and Ammonyx® 490 by Onyx Chemical Company.

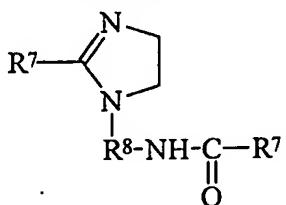
25 **B)-Amine Fabric Softening Active Compound**

Suitable amine fabric softening compounds for use herein, which may be in amine form or cationic form are selected from:

30 (i)- Reaction products of higher fatty acids with a polyamine selected from the group consisting of hydroxyalkylalkylenediamines and dialkylenetriamines and mixtures thereof. These reaction products are mixtures of several compounds in view of the multi-functional structure of the polyamines.

The preferred Component (i) is a nitrogenous compound selected from the group consisting of the reaction product mixtures or some selected components of the mixtures.

5 One preferred component (i) is a compound selected from the group consisting of substituted imidazoline compounds having the formula:



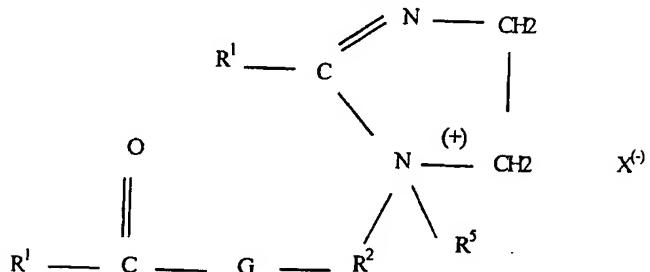
wherein R⁷ is an acyclic aliphatic C₁₅-C₂₁ hydrocarbon group and R⁸ is a divalent C₁-C₃ alkylene group.

10 Component (i) materials are commercially available as: Mazamide® 6, sold by Mazer Chemicals, or Ceranine® HC, sold by Sandoz Colors & Chemicals; stearic hydroxyethyl imidazoline sold under the trade names of Alkazine® ST by Alkaril Chemicals, Inc., or Schercozoline® S by Scher Chemicals, Inc.; N,N"-ditallowalkyldiethylenetriamine; 1-tallowamidoethyl-2-tallowimidazoline (wherein 15 in the preceding structure R¹ is an aliphatic C₁₅-C₁₇ hydrocarbon group and R⁸ is a divalent ethylene group).

20 Certain of the Components (i) can also be first dispersed in a Bronsted acid dispersing aid having a pKa value of not greater than 4; provided that the pH of the final composition is not greater than 6. Some preferred dispersing aids are hydrochloric acid, phosphoric acid, or methylsulfonic acid.

Both N,N"-ditallowalkyldiethylenetriamine and 1-tallow(amidoethyl)-2-tallowimidazoline are reaction products of tallow fatty acids and diethylenetriamine, and are precursors of the cationic fabric softening agent methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate (see "Cationic Surface Active Agents as Fabric Softeners," R. R. Egan, Journal of the American Oil Chemicals' Society, January 1978, pages 118-121). N,N"-ditallow alkoyldiethylenetriamine and 1-tallowamidoethyl-2-tallowimidazoline can be 25 obtained from Witco Chemical Company as experimental chemicals. Methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate is sold by Witco Chemical 30 Company under the tradename Varisoft® 475.

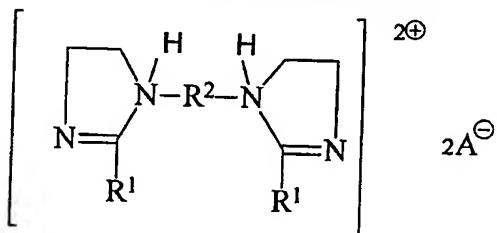
(ii)-softener having the formula:



wherein each R^2 is a C1-6 alkylene group, preferably an ethylene group; and G is an oxygen atom or an -NR- group; and each R, R^1 , R^2 and R^5 have the definitions given above and A^- has the definitions given above for X^- .

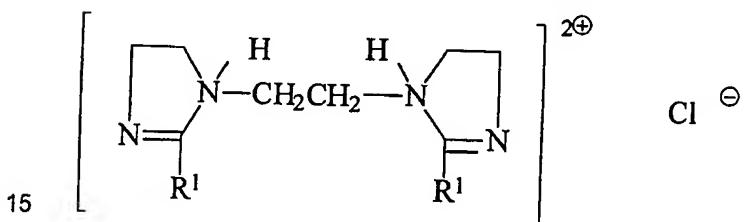
An example of Compound (ii) is 1-oleylamidoethyl-2-oleylimidazolinium chloride wherein R^1 is an acyclic aliphatic C15-C17 hydrocarbon group, R^2 is an ethylene group, G is a NH group, R^5 is a methyl group and A^- is a chloride anion.

10 (iii)- softener having the formula:



wherein R, R^1 , R^2 , and A^- are defined as above.

An example of Compound (iii) is the compound having the formula:



15 wherein R^1 is derived from oleic acid.

Additional fabric softening materials may be used in addition or alternatively to the cationic fabric softener. These may be selected from nonionic, amphoteric or anionic fabric softening material. Disclosure of such materials may be found in
 20 US 4,327,133; US 4,421,792; US 4,426,299; US 4,460,485; US 3,644,203; US

4,661,269; U.S 4,439,335; U.S 3,861,870; US 4,308,151; US 3,886,075; US 4,233,164; US 4,401,578; US 3,974,076; US 4,237,016 and EP 472,178.

Typically, such nonionic fabric softener materials have an HLB of from 2 to 9,
5 more typically from 3 to 7. Such nonionic fabric softener materials tend to be
readily dispersed either by themselves, or when combined with other materials
such as single-long-chain alkyl cationic surfactant described in detail hereinafter.
Dispersibility can be improved by using more single-long-chain alkyl cationic
surfactant, mixture with other materials as set forth hereinafter, use of hotter
10 water, and/or more agitation. In general, the materials selected should be
relatively crystalline, higher melting, (e.g. >40°C) and relatively water-insoluble.

Preferred nonionic softeners are fatty acid partial esters of polyhydric alcohols, or
anhydrides thereof, wherein the alcohol, or anhydride, contains from 2 to 18,
15 preferably from 2 to 8, carbon atoms, and each fatty acid moiety contains from 12
to 30, preferably from 16 to 20, carbon atoms. Typically, such softeners contain
from one to 3, preferably 2 fatty acid groups per molecule.

The polyhydric alcohol portion of the ester can be ethylene glycol, glycerol, poly
20 (e.g., di-, tri-, tetra, penta-, and/or hexa-) glycerol, xylitol, sucrose, erythritol,
pentaerythritol, sorbitol or sorbitan. Sorbitan esters and polyglycerol
monostearate are particularly preferred.

The fatty acid portion of the ester is normally derived from fatty acids having from
25 12 to 30, preferably from 16 to 20, carbon atoms, typical examples of said fatty
acids being lauric acid, myristic acid, palmitic acid, stearic acid and behenic acid.
Highly preferred optional nonionic softening agents for use in the present
invention are the sorbitan esters, which are esterified dehydration products of
sorbitol, and the glycerol esters.

30 Commercial sorbitan monostearate is a suitable material. Mixtures of sorbitan
stearate and sorbitan palmitate having stearate/palmitate weight ratios varying
between 10:1 and 1:10, and 1,5-sorbitan esters are also useful.

Glycerol and polyglycerol esters, especially glycerol, diglycerol, triglycerol, and polyglycerol mono- and/or di-esters, preferably mono-, are preferred herein (e.g. polyglycerol monostearate with a trade name of Radiasurf 7248).

- 5 Useful glycerol and polyglycerol esters include mono-esters with stearic, oleic, palmitic, lauric, isostearic, myristic, and/or behenic acids and the diesters of stearic, oleic, palmitic, lauric, isostearic, behenic, and/or myristic acids. It is understood that the typical mono-ester contains some di- and tri-ester, etc.
- 10 The "glycerol esters" also include the polyglycerol, e.g., diglycerol through octaglycerol esters. The polyglycerol polyols are formed by condensing glycerin or epichlorohydrin together to link the glycerol moieties via ether linkages. The mono- and/or diesters of the polyglycerol polyols are preferred, the fatty acyl groups typically being those described hereinbefore for the sorbitan and glycerol esters.
- 15

Further fabric softening components suitable for use herein are the softening clays, such as the low ion-exchange-capacity ones described in EP-A-0,150,531.

- 20 Of course, the term "softening active" can also encompass mixed softening active agents.
Preferred among the classes of softener compounds disclosed herein before are the diester or diamido quaternary ammonium fabric softening active compound (DEQA).
- 25

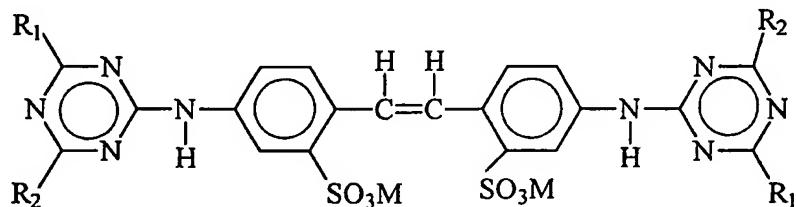
- 30 The fabric softener compounds herein are present at levels of from 1% to 80% of compositions herein, depending on the composition execution which can be dilute with a preferred level of active from 5% to 15%, or concentrated, with a preferred level of active from 15% to 50%, most preferably 15% to 35% by weight of the composition.

- 35 Fully formulated laundry and cleaning compositions such as a softening composition preferably contain, in addition to the hereinbefore described components, one or more of the following ingredients.

(A) Brighteners

The compositions herein can also optionally contain from 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably 5 comprise from 0.001% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl;

10 R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-15 hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX® by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the rinse added compositions herein.

20 When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX® by Ciba-Geigy 25 Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX® by 30 Ciba Geigy Corporation.

(B) Dispersibility Aids

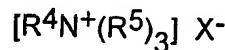
Relatively concentrated compositions containing both saturated and unsaturated diester quaternary ammonium compounds can be prepared that are stable without the addition of concentration aids. However, the compositions of the present invention may require organic and/or inorganic concentration aids to go to even higher concentrations and/or to meet higher stability standards depending on the other ingredients. These concentration aids which typically can be viscosity modifiers may be needed, or preferred, for ensuring stability under extreme conditions when particular softener active levels are used. The surfactant concentration aids are typically selected from the group consisting of (1) single long chain alkyl cationic surfactants; (2) nonionic surfactants; (3) amine oxides; (4) fatty acids; and (5) mixtures thereof. These aids are described in WO 94/20597, specifically on page 14, line 12 to page 20, line 12, which is herein incorporated by reference.

When said dispersibility aids are present, the total level is from 2% to 25%, preferably from 3% to 17%, more preferably from 4% to 15%, and even more preferably from 5% to 13% by weight of the composition. These materials can either be added as part of the active softener raw material, (I), e.g., the mono-long chain alkyl cationic surfactant and/or the fatty acid which are reactants used to form the biodegradable fabric softener active as discussed hereinbefore, or added as a separate component. The total level of dispersibility aid includes any amount that may be present as part of component (I).

(1) Mono-Alkyl Cationic Quaternary Ammonium Compound

When the mono-alkyl cationic quaternary ammonium compound is present, it is typically present at a level of from 2% to 25%, preferably from 3% to 17%, more preferably from 4% to 15%, and even more preferably from 5% to 13% by weight of the composition, the total mono-alkyl cationic quaternary ammonium compound being at least at an effective level.

Such mono-alkyl cationic quaternary ammonium compounds useful in the present invention are, preferably, quaternary ammonium salts of the general formula:



wherein

R^4 is C₈-C₂₂ alkyl or alkenyl group, preferably C₁₀-C₁₈ alkyl or alkenyl group; more preferably C₁₀-C₁₄ or C₁₆-C₁₈ alkyl or alkenyl group;

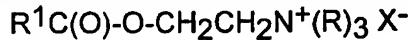
each R⁵ is a C₁-C₆ alkyl or substituted alkyl group (e.g., hydroxy alkyl), preferably C₁-C₃ alkyl group, e.g., methyl (most preferred), ethyl, propyl, and the like, a benzyl group, hydrogen, a polyethoxylated chain with from 2 to 20 oxyethylene units, preferably from 2.5 to 13 oxyethylene units, more preferably from 3 to 10 oxyethylene units, and mixtures thereof; and

5 X⁻ is as defined hereinbefore for (Formula (I)).

Especially preferred dispersibility aids are monolauryl trimethyl ammonium chloride and monotallow trimethyl ammonium chloride available from Witco under the trade names Adogen® 412 and Adogen® 471, monooleyl or monocanola 10 trimethyl ammonium chloride available from Witco under the tradename Adogen® 417, monococonut trimethyl ammonium chloride available from Witco under the trade name Adogen® 461, and monosoya trimethyl ammonium chloride available from Witco under the trade name Adogen® 415.

The R⁴ group can also be attached to the cationic nitrogen atom through a group 15 containing one, or more, ester, amide, ether, amine, etc., linking groups which can be desirable for increased concentratability of component (I), etc. Such linking groups are preferably within from one to three carbon atoms of the nitrogen atom.

Mono-alkyl cationic quaternary ammonium compounds also include C₈-C₂₂ alkyl 20 choline esters. The preferred dispersibility aids of this type have the formula:



wherein R¹, R and X⁻ are as defined previously.

Highly preferred dispersibility aids include C₁₂-C₁₄ coco choline ester and C₁₆-C₁₈ tallow choline ester.

25 Suitable biodegradable single-long-chain alkyl dispersibility aids containing an ester linkage in the long chains are described in U.S. 4,840,738, said patent being incorporated herein by reference.

When the dispersibility aid comprises alkyl choline esters, preferably the compositions also contain a small amount, preferably from 2% to 5% by weight of 30 the composition, of organic acid. Organic acids are described in EP.404,471, which is herein incorporated by reference. Preferably the organic acid is selected from the group consisting of glycolic acid, acetic acid, citric acid, and mixtures thereof.

Ethoxylated quaternary ammonium compounds which can serve as the 35 dispersibility aid include ethylbis(polyethoxy ethanol)alkylammonium ethyl-sulfate with 17 moles of ethylene oxide, available under the trade name Variquat® 66

from Witco Corporation; polyethylene glycol (15) oleammonium chloride, available under the trade name Ethoquad® 0/25 from Akzo; and polyethylene glycol (15) cocomonium chloride, available under the trade name Ethoquad® C/25 from Akzo.

- 5 Quaternary compounds having only a single long alkyl chain, can protect the cationic softener from interacting with anionic surfactants and/or detergent builders that are carried over into the rinse from the wash solution.

(2) Nonionic Surfactant (Alkoxylated Materials)

- 10 Suitable nonionic surfactants to serve as the viscosity/dispersibility modifier include addition products of ethylene oxide and, optionally, propylene oxide, with fatty alcohols, fatty acids, fatty amines, etc. They are referred to herein as ethoxylated fatty alcohols, ethoxylated fatty acids, and ethoxylated fatty amines. Any of the alkoxylated materials of the particular type described hereinafter can
- 15 be used as the nonionic surfactant. In general terms, the nonionics herein, when used alone, in liquid compositions are at a level of from 0% to 5%, preferably from 0.1% to 5%, more preferably from 0.2% to 3%. Suitable compounds are substantially water-soluble surfactants of the general formula:



- 20 wherein R^2 for both solid and liquid compositions is selected from the group consisting of primary, secondary and branched chain alkyl and/or acyl hydrocarbyl groups; primary, secondary and branched chain alkenyl hydrocarbyl groups; and primary, secondary and branched chain alkyl- and alkenyl-substituted phenolic hydrocarbyl groups; said hydrocarbyl groups having
- 25 a hydrocarbyl chain length of from 8 to 20, preferably from 10 to 18 carbon atoms. More preferably the hydrocarbyl chain length for liquid compositions is from 16 to 18 carbon atoms and for solid compositions from 10 to 14 carbon atoms. In the general formula for the ethoxylated nonionic surfactants herein, Y is typically $-O-$, $-C(O)O-$, $-C(O)N(R)-$, or $-C(O)N(R)R-$, preferably $-O-$, and in
- 30 which R^2 , and R, when present, have the meanings given hereinbefore, and/or R can be hydrogen, and z is at least 8, preferably at least 10-11. Performance and, usually, stability of the softener composition decrease when fewer ethoxylate groups are present.
- The nonionic surfactants herein are characterized by an HLB (hydrophilic-lipophilic balance) of from 7 to 20, preferably from 8 to 15. Of course, by defining R^2 and the number of ethoxylate groups, the HLB of the

surfactant is, in general, determined. However, it is to be noted that the nonionic ethoxylated surfactants useful herein, for concentrated liquid compositions, contain relatively long chain R² groups and are relatively highly ethoxylated. While shorter alkyl chain surfactants having short ethoxylated groups can 5 possess the requisite HLB, they are not as effective herein.

Nonionic surfactants as the viscosity/dispersibility modifiers are preferred over the other modifiers disclosed herein for compositions with higher levels of perfume.

Examples of nonionic surfactants follow. The nonionic surfactants of this 10 invention are not limited to these examples. In the examples, the integer defines the number of ethoxy (EO) groups in the molecule.

(3) Amine Oxides

Suitable amine oxides include those with one alkyl or hydroxyalkyl moiety of 8 to 15 22 carbon atoms, preferably from 10 to 18 carbon atoms, more preferably from 8 to 14 carbon atoms, and two alkyl moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups with 1 to 3 carbon atoms.

Examples include dimethyloctylamine oxide, diethyldecylamine oxide, bis-(2-hydroxyethyl)dodecyl-amine oxide, dimethyldodecylamine oxide, dipropyl-20 tetradecylamine oxide, methylethylhexadecylamine oxide, dimethyl-2-hydroxyoctadecylamine oxide, and coconut fatty alkyl dimethylamine oxide.

(C) Stabilizers

Stabilizers can be present in the compositions of the present invention. The term 25 "stabilizer," as used herein, includes antioxidants and reductive agents. These agents are present at a level of from 0% to 2%, preferably from 0.01% to 0.2%, more preferably from 0.035% to 0.1% for antioxidants, and more preferably from 0.01% to 0.2% for reductive agents. These assure good odor stability under long term storage conditions. Antioxidants and reductive agent stabilizers are 30 especially critical for unscented or low scent products (no or low perfume).

Examples of antioxidants that can be added to the compositions of this invention include a mixture of ascorbic acid, ascorbic palmitate, propyl gallate, available from Eastman Chemical Products, Inc., under the trade names Tenox® PG and Tenox® S-1; a mixture of BHT (butylated hydroxytoluene), BHA (butylated 35 hydroxyanisole), propyl gallate, and citric acid, available from Eastman Chemical Products, Inc., under the trade name Tenox®-6; butylated hydroxytoluene, avail-

able from UOP Process Division under the trade name Sustane® BHT; tertiary butylhydroquinone, Eastman Chemical Products, Inc., as Tenox® TBHQ; natural tocopherols, Eastman Chemical Products, Inc., as Tenox® GT-1/GT-2; and butylated hydroxyanisole, Eastman Chemical Products, Inc., as BHA; long chain esters (C_8-C_{22}) of gallic acid, e.g., dodecyl gallate; Irganox® 1010; Irganox® 1035; Irganox® B 1171; Irganox® 1425; Irganox® 3114; Irganox® 3125; and mixtures thereof; preferably Irganox® 3125, Irganox® 1425, Irganox® 3114, and mixtures thereof; more preferably Irganox® 3125 alone or mixed with citric acid and/or other chelators such as isopropyl citrate, Dequest® 2010, available from Monsanto with a chemical name of 1-hydroxyethylidene-1, 1-diphosphonic acid (etidronic acid), and Tiron®, available from Kodak with a chemical name of 4,5-dihydroxy-m-benzene-sulfonic acid/sodium salt, and DTPA®, available from Aldrich with a chemical name of diethylenetriaminepentaacetic acid.

15 (D) Soil Release Agent

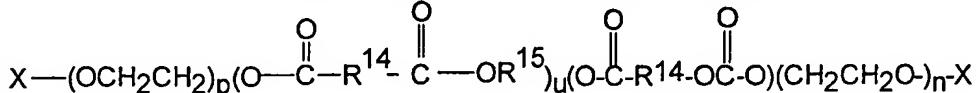
In the present invention, an optional soil release agent can be added. The addition of the soil release agent can occur in combination with the premix, in combination with the acid/water seat, before or after electrolyte addition, or after the final composition is made. The softening composition prepared by the process of the present invention herein can contain from 0% to 10%, preferably from 0.2% to 5%, of a soil release agent. Preferably, such a soil release agent is a polymer. Polymeric soil release agents useful in the present invention include copolymeric blocks of terephthalate and polyethylene oxide or polypropylene oxide, and the like.

25 A preferred soil release agent is a copolymer having blocks of terephthalate and polyethylene oxide. More specifically, these polymers are comprised of repeating units of ethylene terephthalate and polyethylene oxide terephthalate at a molar ratio of ethylene terephthalate units to polyethylene oxide terephthalate units of from 25:75 to 35:65, said polyethylene oxide terephthalate containing 30 polyethylene oxide blocks having molecular weights of from 300 to 2000. The molecular weight of this polymeric soil release agent is in the range of from 5,000 to 55,000.

Another preferred polymeric soil release agent is a crystallizable polyester with repeat units of ethylene terephthalate units containing from 10% to 15% by 35 weight of ethylene terephthalate units together with from 10% to 50% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of

average molecular weight of from 300 to 6,000, and the molar ratio of ethylene terephthalate units to polyoxyethylene terephthalate units in the crystallizable polymeric compound is between 2:1 and 6:1. Examples of this polymer include the commercially available materials Zelcon 4780® (from Dupont) and Milease T 5 ® (from ICI).

Highly preferred soil release agents are polymers of the generic formula:



in which each X can be a suitable capping group, with each X typically being selected from the group consisting of H, and alkyl or acyl groups containing from 10 1 to 4 carbon atoms. p is selected for water solubility and generally is from 6 to 113, preferably from 20 to 50. u is critical to formulation in a liquid composition having a relatively high ionic strength. There should be very little material in which u is greater than 10. Furthermore, there should be at least 20%, preferably at least 40%, of material in which u ranges from 3 to 5.

15 The R¹⁴ moieties are essentially 1,4-phenylene moieties. As used herein, the term "the R¹⁴ moieties are essentially 1,4-phenylene moieties" refers to compounds where the R¹⁴ moieties consist entirely of 1,4-phenylene moieties, or are partially substituted with other arylene or alkarylene moieties, alkylene 20 moieties, alkenylene moieties, or mixtures thereof. Arylene and alkarylene moieties which can be partially substituted for 1,4-phenylene include 1,3-phenylene, 1,2-phenylene, 1,8-naphthylene, 1,4-naphthylene, 2,2-biphenylene, 4,4-biphenylene, and mixtures thereof. Alkylene and alkenylene moieties which 25 can be partially substituted include 1,2-propylene, 1,4-butylene, 1,5-pentylene, 1,6-hexamethylene, 1,7-heptamethylene, 1,8-octamethylene, 1,4-cyclohexylene, and mixtures thereof.

For the R¹⁴ moieties, the degree of partial substitution with moieties other than 30 1,4-phenylene should be such that the soil release properties of the compound are not adversely affected to any great extent. Generally the degree of partial substitution which can be tolerated will depend upon the backbone length of the compound, i.e., longer backbones can have greater partial substitution for 1,4-phenylene moieties. Usually, compounds where the R¹⁴ comprise from 50% to 100% 1,4-phenylene moieties (from 0% to 50% moieties other than 1,4-phenylene) have adequate soil release activity. For example, polyesters made according to the present invention with a 40:60 mole ratio of isophthalic (1,3-phenylene) to terephthalic (1,4-phenylene) acid have adequate soil release 35

activity. However, because most polyesters used in fiber making comprise ethylene terephthalate units, it is usually desirable to minimize the degree of partial substitution with moieties other than 1,4-phenylene for best soil release activity. Preferably, the R¹⁴ moieties consist entirely of (i.e., comprise 100%)

5 1,4-phenylene moieties, i.e., each R¹⁴ moiety is 1,4-phenylene.

For the R¹⁵ moieties, suitable ethylene or substituted ethylene moieties include ethylene, 1,2-propylene, 1,2-butylene, 1,2-hexylene, 3-methoxy-1,2-propylene, and mixtures thereof. Preferably, the R¹⁵ moieties are essentially ethylene moieties, 1,2-propylene moieties, or mixtures thereof. Inclusion of a greater

10 percentage of ethylene moieties tends to improve the soil release activity of compounds. Surprisingly, inclusion of a greater percentage of 1,2-propylene moieties tends to improve the water solubility of compounds.

Therefore, the use of 1,2-propylene moieties or a similar branched equivalent is desirable for incorporation of any substantial part of the soil release component

15 in the liquid fabric softener compositions. Preferably, from 75% to 100%, are 1,2-propylene moieties.

The value for each p is at least 6, and preferably is at least 10. The value for each n usually ranges from 12 to 113. Typically the value for each p is in the range of from 12 to 43.

20 A more complete disclosure of soil release agents is contained in U.S. Pat. Nos.: 4,661,267; 4,711,730; 4,749,596; 4,818,569; 4,877,896; 4,956,447; and 4,976,879, all of said patents being incorporated herein by reference.

These soil release agents can also act as scum dispersants.

25 (E) Scum Dispersant

In the present invention, the premix can be combined with an optional scum dispersant, other than the soil release agent, and heated to a temperature at or above the melting point(s) of the components.

The preferred scum dispersants herein are formed by highly ethoxylating

30 hydrophobic materials. The hydrophobic material can be a fatty alcohol, fatty acid, fatty amine, fatty acid amide, amine oxide, quaternary ammonium compound, or the hydrophobic moieties used to form soil release polymers. The preferred scum dispersants are highly ethoxylated, e.g., more than 17, preferably more than 25, more preferably more than 40, moles of ethylene oxide per

35 molecule on the average, with the polyethylene oxide portion being from 76% to 97%, preferably from 81% to 94%, of the total molecular weight.

The level of scum dispersant is sufficient to keep the scum at an acceptable, preferably unnoticeable to the consumer, level under the conditions of use, but not enough to adversely affect softening. For some purposes it is desirable that the scum is nonexistent. Depending on the amount of anionic or nonionic detergent, etc., used in the wash cycle of a typical laundering process, the efficiency of the rinsing steps prior to the introduction of the compositions herein, and the water hardness, the amount of anionic or nonionic detergent surfactant and detergency builder (especially phosphates and zeolites) entrapped in the fabric (laundry) will vary. Normally, the minimum amount of scum dispersant should be used to avoid adversely affecting softening properties. Typically scum dispersion requires at least 2%, preferably at least 4% (at least 6% and preferably at least 10% for maximum scum avoidance) based upon the level of softener active. However, at levels of 10% (relative to the softener material) or more, one risks loss of softening efficacy of the product especially when the fabrics contain high proportions of nonionic surfactant which has been absorbed during the washing operation.

Preferred scum dispersants are: Brij 700®; Varonic U-250®; Genapol T-500®, Genapol T-800®; Plurafac A-79®; and Neodol 25-50®.

20 (F) Bactericides

Examples of bactericides used in the compositions of this invention include glutaraldehyde, formaldehyde, 2-bromo-2-nitro-propane-1,3-diol sold by Inolex Chemicals, located in Philadelphia, Pennsylvania, under the trade name Bronopol®, and a mixture of 5-chloro-2-methyl-4-isothiazoline-3-one and 2-methyl-4-isothiazoline-3-one sold by Rohm and Haas Company under the trade name Kathon 1 to 1,000 ppm by weight of the agent.

(G) Perfume

The present invention can contain any softener compatible perfume. Suitable perfumes are disclosed in U.S. Pat. 5,500,138, said patent being incorporated herein by reference.

As used herein, perfume includes fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flowers, herbs, leaves, roots, barks, wood, blossoms or plants), artificial (i.e., a mixture of different nature oils or oil constituents) and synthetic (i.e., synthetically produced) odoriferous substances. Such materials are often accompanied by auxiliary materials, such

as fixatives, extenders, stabilizers and solvents. These auxiliaries are also included within the meaning of "perfume", as used herein. Typically, perfumes are complex mixtures of a plurality of organic compounds.

Examples of perfume ingredients useful in the perfumes of the present invention 5 compositions include, but are not limited to, hexyl cinnamic aldehyde; amyl cinnamic aldehyde; amyl salicylate; hexyl salicylate; terpineol; 3,7-dimethyl-*cis*-2,6-octadien-1-ol; 2,6-dimethyl-2-octanol; 2,6-dimethyl-7-octen-2-ol; 3,7-dimethyl-3-octanol; 3,7-dimethyl-*trans*-2,6-octadien-1-ol; 3,7-dimethyl-6-octen-1-ol; 3,7-dimethyl-1-octanol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 4-(4-10 hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; tricyclodecetyl propionate; tricyclodecetyl acetate; anisaldehyde; 2-methyl-2-(para-isopropylphenyl)-propionaldehyde; ethyl-3-methyl-3-phenyl glycidate; 4-(para-hydroxyphenyl)-butan-2-one; 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one; para-methoxyacetophenone; para-methoxy-alpha-phenylpropene; methyl-2-n-15 hexyl-3-oxo-cyclopentane carboxylate; undecalactone gamma.

Additional examples of fragrance materials include, but are not limited to, orange oil; lemon oil; grapefruit oil; bergamot oil; clove oil; dodecalactone gamma; methyl-2-(2-pentyl-3-oxo-cyclopentyl) acetate; beta-naphthol methylether; methyl-beta-naphthylketone; coumarin; decylaldehyde; benzaldehyde; 4-tert-20 butylcyclohexyl acetate; alpha,alpha-dimethylphenethyl acetate; methylphenylcarbinyl acetate; Schiff's base of 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate; cyclic ethyleneglycol diester of tridecanoic acid; 3,7-dimethyl-2,6-octadiene-1-nitrile; ionone gamma methyl; ionone alpha; ionone beta; petitgrain; methyl cedrylone; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl-naphthalene; ionone methyl; methyl-1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; benzophenone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal; 7-hydroxy-3,7-dimethyl octanal; 10-undecen-1-al; iso-30 hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecan; cyclopentadecanolide; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane; ambroxane; dodecahydro-3a,6,6,9a-tetramethylnaphtho-[2,1b]furan; cedrol; 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-butene-35 1-ol; caryophyllene alcohol; cedryl acetate; para-tert-butylcyclohexyl acetate; patchouli; olibanum resinoid; labdanum; vetivert; copaiba balsam; fir balsam; and

condensation products of: hydroxycitronellal and methyl anthranilate; hydroxycitronellal and indol; phenyl acetaldehyde and indol; 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate.

More examples of perfume components are geraniol; geranyl acetate; linalool; 5 linalyl acetate; tetrahydrolinalool; citronellol; citronellyl acetate; dihydromyrcenol; dihydromyrcenyl acetate; tetrahydromyrcenol; terpinyl acetate; nopol; nopyl acetate; 2-phenylethanol; 2-phenylethyl acetate; benzyl alcohol; benzyl acetate; benzyl salicylate; benzyl benzoate; styrallyl acetate; dimethylbenzylcarbinol; trichloromethylphenylcarbinyl methylphenylcarbinyl acetate; isononyl acetate; 10 vetiveryl acetate; vetiverol; 2-methyl-3-(p-tert-butylphenyl)-propanal; 2-methyl-3-(p-isopropylphenyl)-propanal; 3-(p-tert-butylphenyl)-propanal; 4-(4-methyl-3-pentenyl)-3-cyclohexenecarbaldehyde; 4-acetoxy-3-pentyltetrahydropyran; methyl dihydrojasmonate; 2-n-heptylcyclopentanone; 3-methyl-2-pentylcyclopentanone; n-decanal; n-dodecanal; 9-decenol-1; phenoxyethyl isobutyrate; 15 phenylacetaldehyde dimethylacetal; phenylacetaldehyde diethylacetal; geranonitrile; citronellonitrile; cedryl acetal; 3-isocamphylcyclohexanol; cedryl methylether; isolongifolanone; aubepine nitrile; aubepine; heliotropine; eugenol; vanillin; diphenyl oxide; hydroxycitronellal ionones; methyl ionones; isomethyl ionomes; irones; cis-3-hexenol and esters thereof; indane musk fragrances; 20 tetralin musk fragrances; isochroman musk fragrances; macrocyclic ketones; macrolactone musk fragrances; ethylene brassylate.

The perfumes useful in the present invention compositions are substantially free of halogenated materials and nitromusks.

Suitable solvents, diluents or carriers for perfumes ingredients mentioned above 25 are for examples, ethanol, isopropanol, diethylene glycol, monoethyl ether, dipropylene glycol, diethyl phthalate, triethyl citrate, etc. The amount of such solvents, diluents or carriers incorporated in the perfumes is preferably kept to the minimum needed to provide a homogeneous perfume solution.

Perfume can be present at a level of from 0% to 10%, preferably from 0.1% to 30 5%, and more preferably from 0.2% to 3%, by weight of the finished composition. Fabric softener compositions of the present invention provide improved fabric perfume deposition.

(H) Chelating Agents

35 The compositions and processes herein can optionally employ one or more copper and/or nickel chelating agents ("chelators"). Such water-soluble chelating

agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof, all as hereinafter defined. The whiteness and/or brightness of fabrics are substantially improved or restored by such chelating agents and the 5 stability of the materials in the compositions are improved.

Amino carboxylates useful as chelating agents herein include ethylenediaminetetraacetates (EDTA), N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates (NTA), ethylenediamine tetrapropionates, ethylenediamine-N,N'-diglutamates, 2-hydroxypropylenediamine-N,N'-disuccinates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates (DETPA), and ethanoldiglycines, including their water-soluble salts such as the alkali metal, ammonium, and substituted ammonium salts thereof and mixtures thereof.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are 10 permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates), diethylenetriamine-N,N,N',N",N"-pentakis(methane phosphonate) (DETMP) and 1-hydroxyethane-1,1-diphosphonate (HEDP). Preferably, these amino phosphonates to not contain alkyl or alkenyl groups with 15 more than 6 carbon atoms.

The chelating agents are typically used in the present rinse process at levels 20 from 2 ppm to 25 ppm, for periods from 1 minute up to several hours' soaking. The preferred EDDS chelator used herein (also known as ethylenediamine-N,N'-disuccinate) is the material described in U.S. Patent 4,704,233.

As can be seen from the foregoing, a wide variety of chelators can be used 25 herein. Indeed, simple polycarboxylates such as citrate, oxydisuccinate, and the like, can also be used, although such chelators are not as effective as the amino carboxylates and phosphonates, on a weight basis. Accordingly, usage levels may be adjusted to take into account differing degrees of chelating effectiveness. The chelators herein will preferably have a stability constant (of the fully ionized 30 chelator) for copper ions of at least 5, preferably at least 7. Typically, the chelators will comprise from 0.5% to 10%, more preferably from 0.75% to 5%, by weight of the compositions herein. Preferred chelators include DETMP, DETPA, NTA, EDDS and mixtures thereof.

(I)-Enzyme

The compositions and processes herein can optionally employ one or more enzymes such as lipases, proteases, cellulase, amylases and peroxidases. A preferred enzyme for use herein is a cellulase enzyme. Indeed, this type of
5 enzyme will further provide a color care benefit to the treated fabric. Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307 discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted
10 from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® and CELLUZYME® (Novo) are especially useful. Other suitable cellulases are also disclosed in WO 91/17243 to Novo, WO 96/34092, WO 96/34945 and EP-A-0,739,982. In practical terms for current
15 commercial preparations, typical amounts are up to 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. In the particular cases where activity of the enzyme preparation can
20 be defined otherwise such as with cellulases, corresponding activity units are preferred (e.g. CEVU or cellulase Equivalent Viscosity Units). For instance, the compositions of the present invention can contain cellulase enzymes at a level equivalent to an activity from 0.5 to 1000 CEVU/gram of composition. Cellulase enzyme preparations used for the purpose of formulating the compositions of this
25 invention typically have an activity comprised between 1,000 and 10,000 CEVU/gram in liquid form, around 1,000 CEVU/gram in solid form.

(J) Liquid carrier

Another optional, but preferred, ingredient is a liquid carrier. The liquid carrier
30 employed in the instant compositions is preferably at least primarily water due to its low cost, relative availability, safety, and environmental compatibility. The level of water in the liquid carrier is preferably at least 50%, most preferably at least 60%, by weight of the carrier. Mixtures of water and low molecular weight, e.g., <200, organic solvent, e.g., lower alcohols such as ethanol, propanol,
35 isopropanol or butanol are useful as the carrier liquid. Low molecular weight

alcohols include monohydric, dihydric (glycol, etc.) trihydric (glycerol, etc.), and higher polyhydric (polyols) alcohols.

(K) Other Optional Ingredients

5 The present invention can include optional components conventionally used in textile treatment compositions, for example: colorants; preservatives; surfactants; anti-shrinkage agents; fabric crisping agents; spotting agents; germicides; fungicides; anti-oxidants such as butylated hydroxy toluene, anti-corrosion agents, and the like.

10 The present invention can also include other compatible ingredients, including those as disclosed in WO96/02625, WO96/21714, and WO96/21715. Various other optional adjunct ingredients may also be used to provide fully-formulated detergent compositions. The following ingredients are described for the convenience of the formulator, but are not intended to be limiting thereof.

15

Detergent Surfactants

Non-limiting examples of surfactants useful herein typically at levels from 1% to 55%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺)CH₃ and CH₃(CH₂)_y(CHOSO₃⁻M⁺)CH₂CH₃ where x and (y + 1) are integers of at least 7, preferably at least 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially x up to 7 EO ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-C₁₈ glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propanoate), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, cationic surfactants and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides,

such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful.

5 Other conventional useful surfactants are listed in standard texts.

Builders

Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be

10 Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will

15 typically comprise at least 1% builder, preferably from 1% to 80%. Liquid formulations typically comprise from 5% to 50%, more typically 5% to 30%, by weight, of detergent builder. Granular formulations typically comprise from 1% to 80%, more typically from 5% to 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

20 Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However,

25 non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate

30 builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO₂:Na₂O ratio in the range 1.0:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. 4,664,839. NaSKS-6 is the

35 trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate

builder does not contain aluminum. NaSKS-6 has the delta-Na₂SiO₅ morphology form of layered silicate. It can be prepared by methods such as those described in DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the

5 general formula NaMSi_xO_{2x+1}·yH₂O wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na₂SiO₅ (NaSKS-6 form) is most preferred for use herein.

10 Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in DE 2,321,001.

15 Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the

20 empirical formula:

$$M_{z/n}[(AlO_2)_z(SiO_2)_y] \cdot xH_2O$$

wherein z and y are integers usually of at least 6, the molar ratio of z to y is in the range from 1.0 to 0, and x is an integer from 0 to 264, and M is a Group IA or IIA element, e.g., Na, K, Mg, Ca with valence n.

25 Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. 3,985,669.

30 Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:
$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$$

wherein x is from 20 to 30, especially 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of 0.1-10 microns in diameter.

- 5 Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in
10 the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the
15 ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. 3,128,287, U.S. 3,635,830. See also "TMS/TDS" builders of U.S. 4,663,071. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

- 20 Other useful detersity builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, pyromellitic, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.
- 25 Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are
30 also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is 5 dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in EP 0,200,263.

10 Other suitable polycarboxylates are disclosed in U.S. 4,144,226 and in U.S. 3,308,067. See also U.S. 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids such as oleic acid and/or its salts, can also be incorporated into the compositions alone, or in combination 15 with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the 20 formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 25 3,422,137) can also be used.

Bleaching Compounds - Bleaching Agents and Bleach Activators

The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach 30 activators. When present, bleaching agents will typically be at levels of from 1% to 30%, more typically from 5% to 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from 0.1% to 60%, more typically from 0.5% to 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or 5 tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate 10 hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S 4,483,781, U.S 740,446, EP 0,133,354, and U.S 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S 4,634,551.

15 Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, 20 manufactured commercially by DuPont) can also be used.

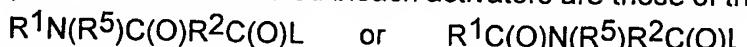
A preferred percarbonate bleach comprises dry particles having an average particle size in the range from 500 micrometers to 1,000 micrometers, not more than 10% by weight of said particles being smaller than 200 micrometers and not 25 more than 10% by weight of said particles being larger than 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

30 Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid 35 corresponding to the bleach activator. Various non-limiting examples of activators are disclosed in U.S 4,915,854, and U.S 4,412,934. The

nonanoyloxybenzene sulfonate (NOBS), 3,5,5-tri-methyl hexanoyl oxybenzene sulfonate (ISONOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

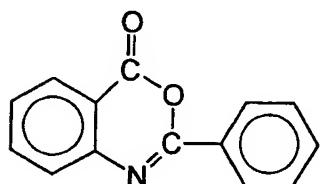
5 Highly preferred amido-derived bleach activators are those of the formulae:



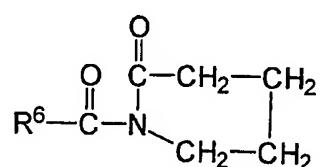
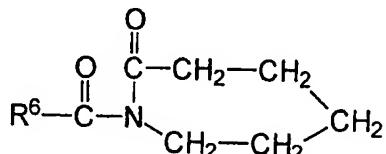
wherein R^1 is an alkyl group containing from 6 to 12 carbon atoms, R^2 is an alkylene containing from 1 to 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from 1 to 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

15 Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzene sulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

20 Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl

valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, 5 including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc 10 and/or aluminum phthalocyanines. See U.S. 4,033,718. If used, detergent compositions will typically contain from 0.025% to 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese 15 compound. Such compounds are well-known in the art and include, for example, the manganese-based catalysts disclosed in U.S. 5,246,621, U.S. 5,244,594; U.S. 5,194,416; U.S. 5,114,606; and EP 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $Mn^{IV}_2(u-O)_3(1,4,7$ -trimethyl-1,4,7-triazacyclononane) $_2(PF_6)_2$, $Mn^{III}_2(u-O)_1(u-OAc)_2(1,4,7$ -trimethyl-1,4,7-triazacyclononane) $_2(ClO_4)_2$, $Mn^{IV}_4(u-O)_6(1,4,7$ -triazacyclononane) $_4(ClO_4)_4$, $Mn^{III}Mn^{IV}_4(u-O)_1(u-OAc)_2(1,4,7$ -trimethyl-1,4,7-triazacyclononane) $_2(ClO_4)_3$, $Mn^{IV}(1,4,7$ -trimethyl-1,4,7-triazacyclononane)- $(OCH_3)_3(PF_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. 5,114,611. The use of 20 manganese with various complex ligands to enhance bleaching is also reported in the following US Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and 30 processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from 0.1 ppm to 700 ppm, more preferably from 1 ppm to 500 ppm, of the catalyst species in the laundry liquor.

35 Other preferred optional ingredients include enzyme stabilisers, polymeric soil release agents, materials effective for inhibiting the transfer of dyes from one

fabric to another during the cleaning process (i.e., dye transfer inhibiting agents), polymeric dispersing agents, suds suppressors, optical brighteners or other brightening or whitening agents, chelating agents, fabric softening clay, anti-static agents, other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations and solid fillers for bar compositions.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monoxylic alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

15 Granular detergents can be prepared, for example, by spray-drying (final product density 520 g/l) or agglomerating (final product density above 600 g/l) the Base Granule. The remaining dry ingredients can then be admixed in granular or powder form with the Base Granule, for example in a rotary mixing drum, and the liquid ingredients (e.g., nonionic surfactant and perfume) can be sprayed on.

20 The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between 6.5 and 11, preferably between 7.5 and 10.5. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well-known to those skilled in the art.

25

Method of use

Also provided herein is a method for providing a delayed release of an active alcohol which comprises the step of contacting the surface to be treated with a material, preferably an aqueous medium comprising a compound or composition of the invention.

30 By "surface", it is meant any surface onto which the compound can deposit. Typical examples of such material are fabrics, hard surfaces such as dishware, floors, bathrooms, toilet, kitchen and other surfaces in need of a delayed release of an active alcohol such as that with litter.

By "delayed release" is meant release of the active component (e.g perfume) over a longer period of time than by the use of the active (e.g., perfume) itself.

5 In the composition examples, the abbreviated component identifications have the following meanings:

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have

10 the following meanings:

DEQA	:	Di-(tallowyl-oxy-ethyl) dimethyl ammonium chloride
DTDMAC	:	Ditallow dimethylammonium chloride
Fatty acid	:	Stearic acid of IV=0
Electrolyte	:	Calcium chloride
PEG	:	Polyethylene Glycol 4000
Carezyme	:	cellulytic enzyme sold by NOVO Industries A/S
LAS	:	Sodium linear C ₁₁ -C ₁₃ alkyl benzene sulfonate
TAS	:	Sodium tallow alkyl sulfate
15 CxyAS	:	Sodium C _{1x} - C _{1y} alkyl sulfate
C46SAS	:	Sodium C ₁₄ - C ₁₆ secondary (2,3) alkyl sulfate
CxyEzS	:	Sodium C _{1x} -C _{1y} alkyl sulfate condensed with z moles of ethylene oxide
20 CxyEz	:	C _{1x} -C _{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide
QAS	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ - C ₁₄
QAS 1	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₈ - C ₁₁
APA	:	C ₈ - C ₁₀ amido propyl dimethyl amine
25 Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut fatty acids
STS	:	Sodium toluene sulphonate
CFAA	:	C ₁₂ -C ₁₄ (coco) alkyl N-methyl glucamide
TFAA	:	C ₁₆ -C ₁₈ alkyl N-methyl glucamide
30 TPKFA	:	C ₁₂ -C ₁₄ topped whole cut fatty acids

	STPP	:	Anhydrous sodium tripolyphosphate
	TSPP	:	Tetrasodium pyrophosphate
	Zeolite A	:	Hydrated sodium aluminosilicate of formula Na ₁₂ (AlO ₂ SiO ₂) ₁₂ .27H ₂ O having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis)
5			
	NaSKS-6	:	Crystalline layered silicate of formula δ- Na ₂ Si ₂ O ₅
10	Citric acid	:	Anhydrous citric acid
	Borate	:	Sodium borate
	Carbonate	:	Anhydrous sodium carbonate with a particle size between 200μm and 900μm
	Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm
15			
	Silicate	:	Amorphous sodium silicate (SiO ₂ :Na ₂ O = 2.0:1)
	Sulfate	:	Anhydrous sodium sulfate
	Mg sulfate	:	Anhydrous magnesium sulfate
	Citrate	:	Tri-sodium citrate dihydrate of activity 86.4%
20			with a particle size distribution between 425μm and 850μm
	MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
	MA/AA (1)	:	Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 10,000
25			
	AA	:	Sodium polyacrylate polymer of average molecular weight 4,500
	CMC	:	Sodium carboxymethyl cellulose
	Cellulose ether	:	Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals
30			
	Protease	:	Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase

	Protease I	:	Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc.
5	Alcalase	:	Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by NOVO Industries A/S
	Cellulase	:	Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme
10	Amylase	:	Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Termamyl 120T
	Lipase	:	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase
15	Lipase (1)	:	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase Ultra
	Endolase	:	Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S
20	PB4	:	Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
	PB1	:	Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
25	Percarbonate	:	Sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
	NOBS	:	Nonanoyloxybenzene sulfonate in the form of the sodium salt
	NAC-OBS	:	(6-nonamidocaproyl) oxybenzene sulfonate
	TAED	:	Tetraacetyl ethylenediamine
30	DTPA	:	Diethylene triamine pentaacetic acid
	DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060
	EDDS	:	Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt.
35			

	Photoactivated (1)	:	Sulfonated zinc phthlocyanine encapsulated in bleach dextrin soluble polymer
	Photoactivated bleach (2)	:	Sulfonated alumino phthlocyanine encapsulated in dextrin soluble polymer
5	Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
	Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5- triazin-2-yl)amino) stilbene-2:2'-disulfonate
	HEDP	:	1,1-hydroxyethane diphosphonic acid
10	PEGx	:	Polyethylene glycol, with a molecular weight of x (typically 4,000)
	PEO	:	Polyethylene oxide, with an average molecular weight of 50,000
	TEPAE	:	Tetraethylenepentaamine ethoxylate
15	VI	:	Polyvinyl imidazole, with an average molecular weight of 20,000
	PVP	:	Polyvinylpyrrolidone polymer, with an average molecular weight of 60,000
	PVNO	:	Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000
20	PVPVI	:	Copolymer of polyvinylpyrrolidone and vinylimidazole, with an average molecular weight of 20,000
	QEA	:	bis((C ₂ H ₅ O)(C ₂ H ₄ O) _n)(CH ₃) -N ⁺ -C ₆ H ₁₂ -N ⁺ - (CH ₃) bis((C ₂ H ₅ O)-(C ₂ H ₄ O)) _n , wherein n = from 20 to 30
25	SRP 1	:	Anionically end capped poly esters
	SRP 2	:	Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
	PEI	:	Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen
30	Silicone antifoam	:	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
35			

Opacifier : Water based monostyrene latex mixture, sold by
BASF Aktiengesellschaft under the tradename
Lytron 621

Wax : Paraffin wax

5

The following are synthesis examples of compounds according to the invention::

I-Synthesis of a copolymer of methyl glyoxylate and dodecanal, end-capped with ethyl vinyl ether

10 Methyl 2-hydroxy-2-methoxyacetate (120 g, 1 mol, 1 eq) is placed in a 250 ml three necks round-bottom flask, fitted with a Vigreux column, a thermometer and a funnel, all glassware having been washed with diluted acid and dried previously. To this is slowly added, in three portions, with stirring, phosphorus pentoxide (71 g, 0.5 mol, 0.5 eq), being careful not to allow the temperature to rise above 90°C. At the end of addition, the mixture is allowed to stir for an hour before heat is applied and the methyl glyoxylate distilled under a nitrogen blanket. 67 g of methyl glyoxylate (bp 106-107°C) is recovered upon distillation. To a solution of freshly distilled methyl glyoxylate (10.2 g, 0.116 mol), dodecanal (10.67 g, 0.058 mol) in dichloromethane (10 ml) is added a freshly made solution of dimethyl sodiomethylmalonate in THF (0.5 ml of a 0.05 mol/l solution). The mixture is stirred at 20°C for an hour then trifluoroacetic acid (0.18 ml, 2.3 mmol) is added, followed by ethyl vinyl ether (3.5 ml, 36.6 mmol). The mixture is stirred at 20°C for 18 hours then sodium carbonate (0.5 g, 4.6 mmol, 2 eq compared to trifluoroacetic acid) is added. The resulting mixture is stirred for 30 minutes before being diluted with 30 ml of dichloromethane and washed with water (25 ml). The aqueous phase is then extracted with dichloromethane (20 ml). Both organic phases are combined and dried over sodium sulfate. After filtration and concentration on the rotaevaporator, a colourless gum (15.5 g) is obtained.

30

II-Synthesis of a copolymer of methyl glyoxylate and trans-4-decenal, end-capped with ethyl vinyl ether

To a solution of freshly distilled methyl glyoxylate (30 g, 0.349 mol), trans-4-decenal (2.63 g, 0.017 mol) in dichloromethane (30 ml) is added boron trifluoride diethyl etherate (1 ml). The mixture is stirred at 0°C for one and a half hour before trifluoroacetic acid (1.08 ml, 14 mmol) is added, followed by a dropwise

addition at 0°C of ethyl vinyl ether (10.5 ml). The mixture is stirred at 20°C for 18 hours then sodium carbonate (1.5 g, 14 mmol) is added. The resulting mixture is stirred for 30 minutes before being diluted with 30 ml of dichloromethane and washed with water (40 ml). The aqueous phase is then extracted with dichloromethane (30 ml). Both organic phases are combined and dried over sodium sulfate. After filtration and concentration on the rotaevaporator, a dark brown gum (30 g) is obtained.

5 III-Synthesis of a terpolymer of methyl glyoxylate, trans-4-decenal and benzaldehyde, end-capped with ethyl vinyl ether

10 To a solution at 0°C of freshly distilled methyl glyoxylate (30 g, 0.349 mol), trans-4-decenal (2.63 g, 0.017 mol) and benzaldehyde (0.19 g, 1.75 mmol) in dichloromethane (30 ml) is added boron trifluoride diethyl etherate (1 ml). The mixture is stirred at 0°C for one and a half hour before trifluoroacetic acid (1.08 ml, 14 mmol) is added, followed by a dropwise addition at 0°C of ethyl vinyl ether (10.5 ml). The mixture is stirred at 0°C for 30 minutes and then at 20°C for 18 hours before sodium carbonate (3 g, 28 mmol) is added. The resulting mixture is stirred for 30 minutes before being diluted with 30 ml of dichloromethane and washed with water (30 ml). The aqueous phase is then extracted with dichloromethane (30 ml). Both organic phases are combined and dried over sodium sulfate. After filtration and concentration on the rotaevaporator, a brown gum (27 g) is obtained.

15 IV-Synthesis of a terpolymer of methyl glyoxylate, methyl nonyl acetaldehyde (2-methyl undecanal), trans-4-decenal and benzaldehyde, end-capped with ethyl vinyl ether

20 To a solution at 0°C of freshly distilled methyl glyoxylate (15 g, 0.17 mol), methyl nonyl acetaldehyde (6.28 g, 34 mmol), trans-4-decenal (1.75 g, 11.4 mmol) and benzaldehyde (1.21 g, 11.4 mmol) in dichloromethane (50 ml) is added boron trifluoride diethyl etherate (0.28 ml, 2.2 mmol). The mixture is stirred at 0°C for one and a half hour before trifluoroacetic acid (1.29 ml, 17 mmol) is added, followed by a dropwise addition at -10°C of ethyl vinyl ether (4 ml, 42 mmol), under nitrogen. The mixture is stirred at -10°C for 30 minutes and then at 20°C for 18 hours, under nitrogen, before sodium carbonate (3 g, 28 mmol) is added.

25 The resulting mixture is stirred for 30 minutes before being diluted with 30 ml of dichloromethane and washed with water (30 ml). The aqueous phase is then

extracted with dichloromethane (30 ml). Both organic phases are combined and dried over sodium sulfate. After filtration and concentration on the rotaevaporator, a straw colour gum (23 g) is obtained.

5 **V-Synthesis of a copolymer of methyl glyoxylate, methyl nonyl acetaldehyde, trans-4-decenal and benzaldehyde, end-capped with ethylene oxide**

To a solution at 0°C of freshly distilled methyl glyoxylate (15 g, 0.17 mol), methyl nonyl acetaldehyde (6.28 g, 34 mmol), trans-4-decenal (1.75 g, 11.4 mmol) and 10 benzaldehyde (1.21 g, 11.4 mmol) in dichloromethane (50 ml) is added boron trifluoride diethyl etherate (0.65 ml, 5.1 mmol). The mixture is stirred at 0°C for two and a half hour before trifluoroacetic acid (0.7 ml, 9 mmol) is added, followed by a dropwise addition at -10°C of ethylene oxide (1.5 ml, 30 mmol), under nitrogen. The mixture is stirred at -10°C for 30 minutes and then at 20°C for 18 15 hours, under nitrogen, before sodium carbonate (1.5 g, 14 mmol) is added. The resulting mixture is stirred for 30 minutes before being diluted with 30 ml of dichloromethane and washed with water (30 ml). The aqueous phase is then extracted with dichloromethane (30 ml). Both organic phases are combined and dried over sodium sulfate. After filtration and concentration on the 20 rotaevaporator, a very light yellow gum (13 g) is obtained.

VI-Synthesis of a copolymer of methyl glyoxylate, methyl nonyl acetaldehyde and trans-4-decenal, end-capped with ethylene oxide

To a solution at 0°C of freshly distilled methyl glyoxylate (15 g, 0.17 mol), methyl 25 nonyl acetaldehyde (8.38 g, 45.5 mmol) and trans-4-decenal (1.75 g, 11.4 mmol) in dichloromethane (50 ml) is added boron trifluoride diethyl etherate (0.65 ml, 5.1 mmol). The mixture is stirred at 0°C for two and a half hour before trifluoroacetic acid (0.7 ml, 9 mmol) is added, followed by a dropwise addition at -10°C of ethylene oxide (1.5 ml, 30 mmol), under nitrogen. The mixture is stirred 30 at -10°C for 30 minutes and then at 20°C for 18 hours, under nitrogen, before sodium carbonate (1.5 g, 14 mmol) is added. The resulting mixture is stirred for 30 minutes before being diluted with 30 ml of dichloromethane and washed with water (30 ml). The aqueous phase is then extracted with dichloromethane (30 ml). Both organic phases are combined and dried over sodium sulfate. After 35 filtration and concentration on the rotaevaporator, a very light yellow gum (19 g) is obtained.

VII-Synthesis of a copolymer of methyl glyoxylate and trans-4-decenal, using phosphorus pentoxide as catalyst

To a solution of freshly distilled methyl glyoxylate (7.96 g, 90 mmol) and trans-4-decenal (4.65 g, 30 mmol) in tetrahydrofuran (30 ml) is added phosphorus pentoxide (1.70 g, 12 mmol). The mixture is stirred under argon at 20°C for 24 hours before removal of the tetrahydrofuran on the rotaevaporator and its replacement with dichloromethane (50 ml). Sodium carbonate (1.0 g, 9.4 mmol) is then added and the resulting mixture is stirred for 30 minutes before being diluted with 30 ml of dichloromethane and washed with water (30 ml). The aqueous phase is then extracted with dichloromethane (30 ml). Both organic phases are combined and dried over magnesium sulfate. After filtration and concentration on the rotaevaporator, a light yellow gum (10.9 g) is obtained.

15 In the following formulation examples all levels are quoted as % by weight of the composition unless otherwise stated:

Example 1

20 The following high density granular laundry detergent compositions A to F were prepared in accord with the invention:

	A	B	C	D	E	F
LAS	8.0	8.0	8.0	2.0	6.0	6.0
TAS	-	0.5	-	0.5	1.0	0.1
C46(S)AS	2.0	2.5	-	-	-	-
C25AS	-	-	-	7.0	4.5	5.5
C68AS	2.0	5.0	7.0	-	-	-
C25E5	-	-	3.4	10.0	4.6	4.6
C25E7	3.4	3.4	1.0	-	-	-
C25E3S	-	-	-	2.0	5.0	4.5
QAS	-	0.8	-	-	-	-
QAS (I)	-	-	-	0.8	0.5	1.0
Zeolite A	18.1	18.0	14.1	18.1	20.0	18.1
Citric acid	-	-	-	2.5	-	2.5
Carbonate	13.0	13.0	27.0	10.0	10.0	13.0

SKS-6	-	-	-	10.0	-	10.0
Silicate	1.4	1.4	3.0	0.3	0.5	0.3
Citrate	-	1.0	-	3.0	-	-
Sulfate	26.1	26.1	26.1	6.0	-	-
Mg sulfate	0.3	-	-	0.2	-	0.2
MA/AA	0.3	0.3	0.3	4.0	1.0	1.0
CMC	0.2	0.2	0.2	0.2	0.4	0.4
PB4	9.0	9.0	5.0	-	-	-
Percarbonate	-	-	-	-	18.0	18.0
TAED	1.5	0.4	1.5	-	3.9	4.2
NAC-OBS	-	2.0	1.0	-	-	-
DTPMP	0.25	0.25	0.25	0.25	-	-
SRP I	-	-	-	0.2	-	0.2
EDDS	-	0.25	0.4	-	0.5	0.5
CFAA	-	1.0	-	2.0	-	-
HEDP	0.3	0.3	0.3	0.3	0.4	0.4
QEA	-	-	-	0.2	-	0.5
Protease I	-	-	0.26	1.0	-	-
Protease	0.26	0.26	-	-	1.5	1.0
Cellulase	0.3	-	-	0.3	0.3	0.3
Amylase	0.1	0.1	0.1	0.4	0.5	0.5
Lipase (1)	0.3	-	-	0.5	0.5	0.5
Photoactivated bleach (ppm)	15 ppm	15 ppm	15 ppm	-	20 ppm	20 ppm
PVNO/PVPVI	-	-	-	0.1	-	-
Brightener 1	0.09	0.09	0.09	-	0.09	0.09
Perfume	0.3	0.3	0.3	0.4	0.4	0.4
Co-polymeric compound (*)	0.3	0.3	0.3	0.4	0.4	0.4
Silicone antifoam	0.5	0.5	0.5	-	0.3	0.3
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

Example 2

The following granular laundry detergent compositions G to L of particular utility under European machine wash conditions were prepared in accord with the invention:

5

	G	H	I	J	K	L
LAS	5.5	7.5	5.0	5.0	6.0	7.0
TAS	1.25	1.86	-	0.8	0.4	0.3
C24AS/C25AS	-	2.24	5.0	5.0	5.0	2.2
C25E3S	-	0.76	1.0	1.5	3.0	1.0
C45E7	3.25	-	-	-	-	3.0
TFAA	-	-	2.0	-	-	-
C25E5	-	5.5	-	-	-	-
QAS	0.8	-	-	-	-	-
QAS II	-	0.7	1.0	0.5	1.0	0.7
STPP	19.7	-	-	-	-	-
Zeolite A	-	19.5	25.0	19.5	20.0	17.0
NaSKS-6/citric acid (79:21)	-	10.6	-	10.6	-	-
NaSKS-6	-	-	9.0	-	10.0	10.0
Carbonate	6.1	21.4	9.0	10.0	10.0	18.0
Bicarbonate	-	2.0	7.0	5.0	-	2.0
Silicate	6.8	-	-	0.3	0.5	-
Citrate	-	-	4.0	4.0	-	-
Sulfate	39.8	-	-	5.0	-	12.0
Mg sulfate	-	-	0.1	0.2	0.2	-
MA/AA	0.5	1.6	3.0	4.0	1.0	1.0
CMC	0.2	0.4	1.0	1.0	0.4	0.4
PB4	5.0	12.7	-	-	-	-
Percarbonate	-	-	-	-	18.0	15.0
TAED	0.5	3.1	-	-	5.0	-
NAC-OBS	1.0	3.5	-	-	-	2.5
DTPMP	0.25	0.2	0.3	0.4	-	0.2
HEDP	-	0.3	-	0.3	0.3	0.3
QEA	-	-	1.0	1.0	1.0	-

Protease I	-	-	-	0.5	1.2	-
Protease	0.26	0.85	0.9	1.0	-	0.7
Lipase (1)	0.15	0.15	0.3	0.3	0.3	0.2
Cellulase	0.28	0.28	0.2	0.2	0.3	0.3
Amylase	0.1	0.1	0.4	0.4	0.6	0.2
PVNO/PVPVI	-	-	0.2	0.2	-	-
PVP	0.9	1.3	-	-	-	0.9
SRP 1	-	-	0.2	0.2	0.2	-
Photoactivated bleach (1) (ppm)	15 ppm	27 ppm	-	-	20 ppm	20 ppm
Photoactivated bleach (2) (ppm)	15 ppm	-	-	-	-	-
Brightener 1	0.08	0.19	-	-	0.09	0.15
Brightener 2	-	0.04	-	-	-	-
Perfume	0.3	0.3	0.4	0.3	0.4	0.3
Co-polymeric compound (*)	0.3	0.3	0.4	0.3	0.4	0.3
Silicone antifoam	0.5	2.4	0.3	0.5	0.3	2.0
Minors/misc to 100%						
Density in g/litre	750	750	750	750	750	750

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

5 Example 3

The following detergent formulations of particular utility under European machine wash conditions were prepared in accord with the invention.

	M	N	O	P
Blown powder				
LAS	6.0	5.0	11.0	6.0
TAS	2.0	-	-	2.0
Zeolite A	24.0	-	-	20.0
STPP	-	27.0	24.0	-
Sulfate	4.0	6.0	13.0	-

MA/AA	1.0	4.0	6.0	2.0
Silicate	1.0	7.0	3.0	3.0
CMC	1.0	1.0	0.5	0.6
Brightener 1	0.2	0.2	0.2	0.2
Silicone antifoam	1.0	1.0	1.0	0.3
DTPMP	0.4	0.4	0.2	0.4
Spray on				
Brightener	0.02	-	-	0.02
C45E7	-	-	-	5.0
C45E2	2.5	2.5	2.0	-
C45E3	2.6	2.5	2.0	-
Perfume	0.5	0.3	0.5	0.2
Co-polymeric compound (*)	0.5	0.3	0.5	0.2
Silicone antifoam	0.3	0.3	0.3	-
Dry additives				
QEA	-	-	-	1.0
EDDS	0.3	-	-	-
Sulfate	2.0	3.0	5.0	10.0
Carbonate	6.0	13.0	15.0	14.0
Citric acid	2.5	-	-	2.0
QAS II	0.5	-	-	0.5
SKS-6	10.0	-	-	-
Percarbonate	18.5	-	-	-
PB4	-	18.0	10.0	21.5
TAED	2.0	2.0	-	2.0
NAC-OBS	3.0	2.0	4.0	-
Protease	1.0	1.0	1.0	1.0
Lipase	-	0.4	-	0.2
Lipase (1)	0.4	-	0.4	-
Amylase	0.2	0.2	0.2	0.4
Brightener 1	0.05	-	-	0.05
Misc/minor to 100%				

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

Example 4

The following granular detergent formulations were prepared in accord with the invention.

5

	Q	R	S	T	U	V
Blown powder						
LAS	23.0	8.0	7.0	9.0	7.0	7.0
TAS	-	-	-	-	1.0	-
C45AS	6.0	6.0	5.0	8.0	-	-
C45AES	-	1.0	1.0	1.0	-	-
C45E35	-	-	-	-	2.0	4.0
Zeolite A	10.0	18.0	14.0	12.0	10.0	10.0
MA/AA	-	0.5	-	-	-	2.0
MA/AA (1)	7.0	-	-	-	-	-
AA	-	3.0	3.0	2.0	3.0	3.0
Sulfate	5.0	6.3	14.3	11.0	15.0	19.3
Silicate	10.0	1.0	1.0	1.0	1.0	1.0
Carbonate	15.0	20.0	10.0	20.7	8.0	6.0
PEG 4000	0.4	1.5	1.5	1.0	1.0	1.0
DTPA	-	0.9	0.5	-	-	0.5
Brightener 2	0.3	0.2	0.3	-	0.1	0.3
Spray on						
C45E7	-	2.0	-	-	2.0	2.0
C25E9	3.0	-	-	-	-	-
C23E9	-	-	1.5	2.0	-	2.0
Perfume	0.3	0.3	0.3	2.0	0.3	0.3
Co-polymeric compound (*)	0.3	0.3	0.3	2.0	0.3	0.3
Agglomerates						
C45AS	-	5.0	5.0	2.0	-	5.0
LAS	-	2.0	2.0	-	-	2.0
Zeolite A	-	7.5	7.5	8.0	-	7.5
Carbonate	-	4.0	4.0	5.0	-	4.0
PEG 4000	-	0.5	0.5	-	-	0.5

Misc (water etc.)	-	2.0	2.0	2.0	-	2.0
Dry additives						
QAS (I)	-	-	-	-	1.0	-
Citric acid	-	-	-	-	2.0	-
PB4	-	-	-	-	12.0	1.0
PB1	4.0	1.0	3.0	2.0	-	-
Percarbonate	-	-	-	-	2.0	10.0
Carbonate	-	5.3	1.8	-	4.0	4.0
NOBS	4.0	-	6.0	-	-	0.6
Methyl cellulose	0.2	-	-	-	-	-
SKS-6	8.0	-	-	-	-	-
STS	-	-	2.0	-	1.0	-
Cumene sulfonic acid	-	1.0	-	-	-	2.0
Lipase	0.2	-	0.2	-	0.2	0.4
Cellulase	0.2	0.2	0.2	0.3	0.2	0.2
Amylase	0.2	-	0.1	-	0.2	-
Protease	0.5	0.5	0.5	0.3	0.5	0.5
PVPVI	-	-	-	-	0.5	0.1
PVP	-	-	-	-	0.5	-
PVNO	-	-	0.5	0.3	-	-
QEA	-	-	-	-	1.0	-
SRP1	0.2	0.5	0.3	-	0.2	-
Silicone antifoam	0.2	0.4	0.2	0.4	0.1	-
Mg sulfate	-	-	0.2	-	0.2	-
Misc/minors to 100%						

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

Example 5

The following nil bleach-containing detergent formulations of particular use in the
5 washing of coloured clothing, according to the present invention were prepared:

	W	X	Y
Blown Powder			
Zeolite A	15.0	15.0	-
Sulfate	0.0	5.0	-

LAS	3.0	3.0	-
DTPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
Zeolite A	10.0	15.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0
Spray On			
Perfume	0.3	0.3	0.5
Co-polymeric compound (*)	0.3	0.3	0.5
C45E7	4.0	4.0	4.0
C25E3	2.0	2.0	2.0
Dry additives			
MA/AA	-	-	3.0
NaSKS-6	-	-	12.0
Citrate	10.0	-	8.0
Bicarbonate	7.0	3.0	5.0
Carbonate	8.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Alcalase	0.5	0.3	0.9
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sulfate	0.0	9.0	0.0
Misc/minors to 100%	100.0	100.0	100.0
Density (g/litre)	700	700	700

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

Example 6

The following granular detergent formulations were prepared in accord with the invention.

5

	Z	AA	BB
Base granule			
Zeolite A	30.0	22.0	24.0
Sulfate	10.0	5.0	10.0
MA/AA	3.0	-	-
AA	-	1.6	2.0
MA/AA (1)	-	12.0	-
LAS	14.0	10.0	9.0
C45AS	8.0	7.0	9.0
C45AES	-	1.0	1.0
Silicate	-	1.0	0.5
Soap	-	2.0	-
Brightener 1	0.2	0.2	0.2
Carbonate	6.0	9.0	10.0
PEG 4000	-	1.0	1.5
DTPA	-	0.4	-
Spray on			
C25E9	-	-	-
C45E7	1.0	1.0	-
C23E9	-	1.0	2.5
Perfume	0.2	0.3	0.3
Co-polymeric compound (*)	0.2	0.3	0.3
Dry additives			
Carbonate	5.0	10.0	18.0
PVPVI/PVNO	0.5	-	0.3
Protease	1.0	1.0	1.0
Lipase	0.4	-	-
Amylase	0.1	-	-
Cellulase	0.1	0.2	0.2
NOBS	-	4.0	-

PB1	1.0	5.0	1.5
Sulfate	4.0	5.0	-
SRPI	-	0.4	-
Sud supressor	-	0.5	0.5
Misc/minor to 100%			

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

5 Example 7

The following granular detergent compositions were prepared in accord with the invention.

	CC	DD	EE
Blown powder			
Zeolite A	20.0	-	15.0
STPP	-	20.0	-
Sulphate	-	-	5.0
Carbonate	-	-	5.0
TAS	-	-	1.0
LAS	6.0	6.0	6.0
C68AS	2.0	2.0	-
Silicate	3.0	8.0	-
MA/AA	4.0	2.0	2.0
CMC	0.6	0.6	0.2
Brightener 1	0.2	0.2	0.1
DTPMP	0.4	0.4	0.1
STS	-	-	1.0
Spray on			
C45E7	5.0	5.0	4.0
Silicone antifoam	0.3	0.3	0.1
Perfume	0.2	0.2	0.3
Co-polymeric compound (*)	0.2	0.2	0.3
Dry additives			
QEА	-	-	1.0

Carbonate	14.0	9.0	10.0
PB1	1.5	2.0	-
PB4	18.5	13.0	13.0
TAED	2.0	2.0	2.0
QAS (I)	-	-	1.0
Photoactivated bleach	15 ppm	15 ppm	15ppm
SKS-6	-	-	3.0
Protease	1.0	1.0	0.2
Lipase	0.2	0.2	0.2
Amylase	0.4	0.4	0.2
Cellulase	0.1	0.1	0.2
Sulfate	10.0	20.0	5.0
Misc/minors to 100%			
Density (g/litre)	700	700	700

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

Example 8

The following detergent compositions, according to the present invention were
5 prepared:

	FF	GG	HH
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DTPMP	0.4	0.2	0.4
EDDS	-	0.4	0.2
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0

	Carbonate	8.0	8.0	4.0
Spray On				
Perfume	0.3	0.3	0.3	
Co-polymeric compound (*)	0.3	0.3	0.3	
C45E7	2.0	2.0	2.0	
C25E3	2.0	-	-	
Dry additives				
Citrate	5.0	-	2.0	
Bicarbonate	-	3.0	-	
Carbonate	8.0	15.0	10.0	
TAED	6.0	2.0	5.0	
PB1	14.0	7.0	10.0	
PEO	-	-	0.2	
Bentonite clay	-	-	10.0	
Protease	1.0	1.0	1.0	
Lipase	0.4	0.4	0.4	
Amylase	0.6	0.6	0.6	
Cellulase	0.6	0.6	0.6	
Silicone antifoam	5.0	5.0	5.0	
Dry additives				
Sodium sulfate	0.0	3.0	0.0	
Misc/minors to 100%	100.0	100.0	100.0	
Density (g/litre)	850	850	850	

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

Example 9

5 The following detergent formulations, according to the present invention were prepared:

	II	JJ	KK	LL
LAS	20.0	14.0	24.0	20.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C23E56.5	-	-	1.0	-

C45E7	-	1.0	-	-
C45E3S	1.0	2.5	1.0	-
STPP	36.0	18.0	30.0	22.0
Silicate	9.0	5.0	9.0	8.0
Carbonate	13.0	7.5	10.0	5.0
Bicarbonate	-	7.5	-	-
PB1	3.0	1.0	-	-
PB4	-	1.0	-	-
NOBS	2.0	1.0	-	-
DTPMP	-	1.0	-	-
DTPA	0.5	-	0.2	0.3
SRP 1	0.3	0.2	-	0.1
MA/AA	1.0	1.5	2.0	0.5
CMC	0.8	0.4	0.4	0.2
PEI	-	-	0.4	-
Sodium sulfate	25.0	10.0	20.0	30.0
Mg sulfate	0.2	-	0.4	0.9
Protease	0.8	1.0	0.5	0.5
Amylase	0.5	0.4	-	0.25
Lipase	0.2	-	0.1	-
Cellulase	0.15	-	-	0.05
Photoactivated bleach (ppm)	30ppm	20ppm	-	10ppm
Perfume	0.3	0.3	0.1	0.2
Co-polymeric compound (*)	0.3	0.3	0.1	0.2
Brightener 1/2	0.05	0.2	0.08	0.1
Misc/minors to 100%				

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

Example 10

The following liquid detergent formulations were prepared in accord with the invention (levels are given as parts per weight).

5

	MM	NN	OO	PP	QQ
LAS	11.5	8.8	-	3.9	-
C25E2.5S	-	3.0	18.0	-	16.0
C45E2.25S	11.5	3.0	-	15.7	-
C23E9	-	2.7	1.8	2.0	1.0
C23E7	3.2	-	-	-	-
CFAA	-	-	5.2	-	3.1
TPKFA	1.6	-	2.0	0.5	2.0
Citric acid (50%)	6.5	1.2	2.5	4.4	2.5
Calcium formate	0.1	0.06	0.1	-	-
Sodium formate	0.5	0.06	0.1	0.05	0.05
Sodium cumene sulfonate	4.0	1.0	3.0	1.18	-
Borate	0.6	-	3.0	2.0	2.9
Sodium hydroxide	5.8	2.0	3.5	3.7	2.7
Ethanol	1.75	1.0	3.6	4.2	2.9
1, 2 propanediol	3.3	2.0	8.0	7.9	5.3
Monoethanolamine	3.0	1.5	1.3	2.5	0.8
TEPAE	1.6	-	1.3	1.2	1.2
Protease	1.0	0.3	1.0	0.5	0.7
Lipase	-	-	0.1	-	-
Cellulase	-	-	0.1	0.2	0.05
Amylase	-	-	-	0.1	-
SRP1	0.2	-	0.1	-	-
DTPA	-	-	0.3	-	-
PVNO	-	-	0.3	-	0.2
Brightener 1	0.2	0.07	0.1	-	-
Silicone antifoam	0.04	0.02	0.1	0.1	0.1
Co-polymeric compound (*)	0.04	0.02	0.1	0.1	0.1
Water/minors					

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

Example 11

The following liquid detergent formulations were prepared in accord with the invention (levels are given in parts per weight):

5

	RR	SS	TT	UU	VV
LAS	10.0	13.0	-	25.0	-
C25AS	4.0	1.0	10.0	-	13.0
C25E3S	1.0	-	3.0	-	2.0
C25E7	6.0	8.0	2.5	-	-
TFAA	-	-	4.5	-	6.0
APA	-	1.4	-	3.0	1.0
TPKFA	2.0	-	7.0	-	15.0
Citric acid	2.0	3.0	1.5	1.0	1.0
Dodecenyl/tetradecenyl succinic acid	12.0	10.0	-	15.0	-
Rape seed fatty acid	4.0	2.0	-	1.0	-
Ethanol	4.0	4.0	2.0	7.0	2.0
1,2 Propanediol	4.0	4.0	7.0	6.0	8.0
Monoethanolamine	-	-	5.0	-	-
Triethanolamine	-	-	-	-	-
TEPAE	0.5	-	0.2	-	-
DTPMP	1.0	1.0	1.0	2.0	1.2
Protease	0.5	0.5	0.25	-	0.5
Alcalase	-	-	-	1.5	-
Lipase	-	0.10	0.01	-	-
Amylase	0.25	0.25	0.5	0.25	0.9
Cellulase	-	-	0.05	-	-
Endolase	-	-	0.10	-	-
SRP2	0.3	-	0.1	-	--
Boric acid	0.1	0.2	2.0	1.0	1.5
Calcium chloride	-	0.02	0.01	-	-
Bentonite clay	-	-	-	4.0	4.0
Brightener 1	-	0.4	-	0.1	0.2
Sud suppressor	0.1	0.3	0.1	0.4	-

Opacifier	0.5	0.4	0.3	0.8	0.7
Co-polymeric compound (*)	0.5	0.4	0.3	0.8	0.7
Water/minors to 100%					
NaOH up to pH	8.0	8.0	7.7	8.0	7.5

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

Example 12

5 The following liquid detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

	WW	XX
LAS	27.6	18.9
C45AS	13.8	5.9
C13E8	3.0	3.1
Oleic acid	3.4	2.5
Citric acid	5.4	5.4
Sodium hydroxide	0.4	3.6
Calcium formate	0.2	0.1
Sodium formate	-	0.5
Ethanol	7.0	-
Monoethanolamine	16.5	8.0
1,2 propanediol	5.9	5.5
Xylene sulfonic acid	-	2.4
TEPAE	1.5	0.8
Protease	1.5	0.6
PEG	-	0.7
Brightener 2	0.4	0.1
Perfume	0.5	0.3
Co-polymeric compound (*)	0.5	0.3
Water/minors		

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

Example 13

The following laundry bar detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

5

	YY	ZZ	AB	AC	AD	AE
LAS	-	-	19.0	15.0	21.0	-
C28AS	30.0	13.5	-	-	-	22.5
Sodium laurate	2.5	9.0	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25
Carbonate	20.0	3.0	13.0	8.0	10.0	10.0
Calcium carbonate	27.5	39.0	35.0	-	-	40.0
Sulfate	5.0	5.0	3.0	5.0	3.0	5.0
TSPP	5.0	-	-	-	-	-
STPP	5.0	15.0	10.0	-	-	10.0
Bentonite clay	-	10.0	-	-	5.0	-
DTPMP	-	0.7	0.6	-	0.6	0.7
CMC	-	1.0	1.0	1.0	1.0	1.0
Talc	-	-	10.0	15.0	10.0	-
Silicate	-	-	4.0	5.0	3.0	-
PVNO	0.02	0.03	-	0.01	-	-
MA/AA	0.4	1.0	-	-	0.2	0.4
SRP1	0.3	0.3	0.3	0.3	0.3	0.3
Protease	-	0.12	-	0.08	0.08	0.1
Lipase	-	0.1	-	0.1	-	-
Amylase	-	-	0.8	-	-	-
Cellulase	-	0.15	-	-	0.15	-
PEO	-	0.2	-	0.2	0.3	0.3
Perfume	1.0	0.5	0.3	0.2	0.4	0.4
Co-polymeric compound (*)	1.0	0.5	0.3	0.2	0.4	0.4
Mg sulfate	-	-	3.0	3.0	3.0	-
Brightener	0.15	0.10	0.15	-	-	0.1
Photoactivated bleach (ppm)	-	15.0	15.0	15.0	15.0	15.0

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

Example 14

The following fabric softening compositions are in accordance with the present invention

Component	AF	AG	AH	AI	AJ	AK
DTDMAC	-	-	-	-	4.5	15.0
DEQA	2.6	2.9	18.0	19.0	-	-
Fatty acid	0.3	-	1.0	-	-	-
Hydrochloride acid	0.02	0.02	0.02	0.02	0.02	0.02
PEG	-	-	0.6	0.6	-	0.6
Perfume	1.0	1.0	1.0	1.0	1.0	1.0
Silicone antifoam	0.01	0.01	0.01	0.01	0.01	0.01
Co-polymeric compound (*)	0.4	0.6	0.8	0.8	0.6	0.8
Electrolyte (ppm)	-	-	600	1200	-	1200
Dye (ppm)	10	10	50	50	10	50
Carezyme CEVU/g	-	-	-	50	-	-
Water and minors to balance to 100						

5 (*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

Example 15

The following compositions for use as dryer-added sheets are in accordance with the invention

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	AL	AM	AN	AO	AP	AQ
DOEQA	40	25	-	-	-	-
DHEQA	-	-	20	-	-	-
DTDMAMS	-	-	-	20	12	60
SDASA	30	30	20	30	20	-
Glycosperse S-20	-	-	10	-	-	-
Glycerol Monostearate	-	-	-	20	10	-
Clay	4	4	3	4	4	-
Perfume	0.7	1.1	0.7	1.6	2.6	1.4

Co-polymeric compound (*)	0.8	0.5	0.8	0.8	0.5	1.20
Stearic acid to balance						

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

Example 16

5 The following hard surface cleaning compositions AX to AZ are in accordance with the present invention

	AR	AS	AT
Dobanol 23-3®	3.20	3.20	1.28
Lutensol AO30®	4.80	4.80	1.92
Dobanol C7-11EO6®	8.0	8.0	3.20
Topped Palm Kernel Fatty acid, Na salt	0.80	0.80	0.40
C8 Alkyl sulphate, Na salt	2.0	2.0	0.8
Parafin sulphonate, Na salt	3.0	3.0	1.20
Cumene sulphonate, Na salt	3.0	3.0	1.20
Perfume	0.8	0.8	0.6
Branched alcohol, Isofol 16®	-	-	0.30
Co-polymeric compound (*)	1.86	2.49	0.6
NaOH up to	pH 10	pH 10	pH 10
Water and Minors up to 100%			

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

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Example 17

The following dishwashing machine compositions according to the invention were prepared.

	AU	AV	AW	AX	AY	AZ	BA
Citrate	15.0	15.0	15.0	15.0	15.0	15.0	-
480N	6.0	6.0	6.0	6.0	6.0	6.0	-
Carbonate	17.5	17.5	17.5	17.5	17.5	17.5	-
STPP	-	-	-	-	-	-	38.0

Silicate (as SiO ₂)	8.0	8.0	8.0	8.0	8.0	8.0	14.0
Metasilicate (as SiO ₂)	1.2	1.2	1.2	1.2	1.2	1.2	2.5
PB1 (AvO)	1.2	1.2	1.5	1.5	1.5	2.2	1.2
TAED	2.2	2.2	2.2	-	-	2.2	2.2
BzP	-	-	-	0.8	-	-	-
Cationic precursor	-	-	-	-	3.3	-	-
Paraffin	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Bismuth nitrate	-	0.2	0.2	0.2	0.3	0.4	0.2
BD/MA	-	-	-	-	-	-	0.5
PMT	-	-	-	-	-	-	0.5
Protease	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Amylase	0.03	0.03	0.03	0.03	0.03	0.03	-
BSA	-	-	-	-	-	-	0.03
DETPMP	0.13	0.13	0.13	0.13	0.13	0.13	-
HEDP	1.0	1.0	1.0	1.0	1.0	1.0	-
Nonionic	2.0	2.0	2.0	2.0	2.0	2.0	1.5
Co-polymeric compound (*)	0.5	0.5	0.5	1.86	1.86	1.86	1.86
Sulphate	23.0	22.8	22.4	22.7	22.2	21.5	0.3
misc inc Moisture to balance							

(*) Co-polymeric compound as made in any one of Synthesis Examples I to VII.

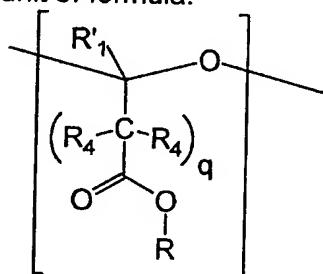
Claims

1- A co-polymeric compound having the following empirical formula:

-[Y_m-A_n]-

wherein Y is a comonomeric aldehyde unit of formula R'COH,
 wherein R' is the organic chain of an active aldehyde,
 wherein A is a co-monomeric unit capable of polymerising the aldehyde monomeric unit,
 wherein n and m are each independently indexes of value of at least 1, preferably less than 1000, most preferably less than 100.

2- A compound according to Claim 1, wherein A is a keto carboxylate monomeric unit of formula:



wherein each R is independently selected from hydrogen, alkali metals, ammonium, alkyl, alkylene, aryl, alkylaryl, or any other chain containing at least 1 carbon atom;

wherein each R'1 is independently selected from hydrogen, hydroxyl, alkyl, alkylene, aryl, alkylaryl, COOR3, (CR₄R₄)_qCOOR3, OR3, or any other chains containing at least 1 carbon atom;

wherein each R3 is independently selected from hydrogen, alkali metals, ammonium, alkyl, alkylene, aryl, alkylaryl, or any other chain containing at least 1 carbon atom, and

wherein each R4 are independently selected from hydrogen, hydroxyl, alkyl, alkylene, aryl, alkylaryl, COOR3, CH₂COOR3, OR3, or any other chain containing at least 1 carbon atom; and

wherein q is from 0 to 10, preferably from 0 to 4, more preferably 0, 1 or 2.

3- A compound according to Claim 1, wherein A is a glyoxylic monomeric unit of formula:

wherein each R is independently selected from hydrogen, alkali metals, ammonium, alkyl, alkylene, aryl, alkylaryl, or any other chain containing at least 1 carbon atom;

wherein each R'1 is independently selected from hydrogen, hydroxyl, alkyl, alkylene, aryl, alkylaryl, COOR3, OR3, or any other chains containing at least 1 carbon atom;

wherein each R3 is independently selected from hydrogen, alkali metals, ammonium, alkyl, alkylene, aryl, alkylaryl, or any other chain containing at least 1 carbon atom, and

wherein q is 0.

4-A compound according to either one of Claim 2 or 3, wherein each R is independently selected from alkali metals, ammonium, C1-C6 alkyl chains, and more preferably are selected from methyl and ethyl.

5-A compound according to any one of Claims 2-4, wherein each R'1 is independently selected from hydrogen, -COOR3, $(CR_4R_4)_qCOOR_3$, aryl group, and C1-C6 alkyl chains, and more preferably are selected from hydrogen, -COOR3, phenyl, methyl and ethyl.

6-A compound according to any one of Claims 2-5, wherein each R3 groups is independently selected from hydrogen, alkali metals, ammonium, aryl group and C1-C6 alkyl chains, and more preferably are selected from hydrogen, alkali metals, ammonium, methyl and ethyl.

7-A compound according to any one of Claims 2-6, wherein each R4 is independently selected from hydrogen, -COOR3, aryl group and C1-C6 alkyl chains, and more preferably is selected from hydrogen, phenyl, methyl and ethyl.

8-A compound according to any one of Claims 1-7, wherein said co-polymer comprises one or more end-capping groups selected from alkyl or alkoxy groups

containing oxygen, preferably selected from -CH₂CHOH, -CH(CH₃)-O-CH₂CH₃, -OCH₂CHOH and -OCH(CH₃)-O-CH₂CH₃.

9-A compound according to any one of Claims 1-8, wherein said organic chain of an active aldehyde is the organic chain of a perfume aldehyde, preferably selected from 1-octanal, 1-decanal, 1-dodecanal, methylnonyl acetaldehyde, trans-4-decenal, benzaldehyde and mixture thereof.

10-A process for preparing copolymers of active aldehydes and keto carboxylates, preferably copolymers of active aldehydes and glyoxylic compounds, comprising one or more active aldehyde ingredients by

- i) polymerisation of one or more active aldehydes with one or more comonomers capable of polymerising the aldehyde monomeric unit, in presence of a polymerisation initiator;
- ii) End-capping the resulting copolymer, preferably using a catalyst selected from boron trifluoride etherate and trifluoroacetic acid.

11-A laundry and cleaning composition or personal cleansing composition comprising a compound as defined in any one of claims 1-9.

12- A composition according to Claim 11, wherein said compound is incorporated at a level of 0.01% to 10%, preferably from 0.05% to 5%, and more preferably from 0.1% to 2%, by weight of the composition.

13-A composition according to either one of Claims 11 or 12, wherein said composition is a laundry and cleaning composition selected from a fabric softening composition, a detergent composition, a hard surface cleaning composition.

14-A composition according to any one of Claims 11-13, wherein said composition further comprises an enzyme, preferably a cellulase.

15-A method of delivering residual fragrance to a surface which comprises the steps of contacting said surface with a compound as defined in Claim 9 or a composition as defined in any one of Claims 11-14 in presence of a material so

that the perfume aldehydes are slowly released overtime by hydrolysis of the copolymer backbone.

16-A method according to Claim 15, wherein said material is water.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/17836

A. CLASSIFICATION OF SUBJECT MATTER			
IPC 6	C08G2/20	C08G2/30	C11D3/37
			A61K7/46

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G A61K C11D A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 204 052 A (CRUTCHFIELD MARVIN M ET AL) 20 May 1980 see claims 1-33; example 7 -----	1-16

Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
19 June 1998	08/07/1998
Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Stienon, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/17836

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 4204052	A 20-05-1980	BR	7805391 A	08-05-1979
		CA	1107746 A	25-08-1981
		DK	369078 A	23-02-1979
		EP	0001004 A	07-03-1979
		JP	1436550 C	25-04-1988
		JP	54052196 A	24-04-1979
		JP	62037044 B	11-08-1987
		US	4315092 A	09-02-1982
		ZA	7804737 A	29-08-1979

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